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Hydrolytic Reactivity of a Samarium(II) Organometallic Complex: Synthesis and Structure of a Hexametallic Organosamarium Oxide Hydroxide, $[(C_5Me_5)Sm]_6O_9H_6$

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*Summary: Controlled hydrolysis of the divalent organosamarium complex $(C_5Me_5)_2Sm(THF)_2$ in THF forms $[(C_5Me_5)Sm]_6O_9H_6$, **1**, which has a solid-state structure consisting of a distorted octahedral array of six $[(C_5Me_5)Sm]^{2+}$ units connected by eight triply bridging oxygens and a central oxygen.*

Introduction

Although hydrolysis is one of the most common reactions that can occur during the manipulation of organometallic reagents of electropositive metals, surprisingly little is known about the reaction or the reaction products. Hydrolysis of organometallic derivatives of electropositive metals is usually viewed as the conversion of M−R to R−H and "M−OH." However, the nature of the "M−OH" is rarely specified even though the structure and composition of the "M−OH" unit can be important to the subsequent reaction chemistry. For example, a hydroxy metal complex still can function as a Lewis acid and, if M is a trivalent lanthanide and if additional equivalents of R are present, the metal could support other reactive functionalities. Since "$RLi/CeCl_3$" reagent systems often use excess RLi and often start with partially hydrated cerium chloride,[1] it is of interest to gain a better understanding of Ln−R hydrolysis reactions. This is also of interest regarding $SmI_2(THF)_x$ reactions, which are often postulated to involve Sm−R bonds which subsequently get hydrolyzed[2−6] during product isolation procedures.

We report here on the reaction of water with the Sm(II) organometallic complex $(C_5Me_5)_2Sm(THF)_2$.[7] This specific complex was chosen since the C_5Me_5 ligands often provide more tractable and identifiable products than alkyl ligands and offer a better chance of isolating a "M−OH" product. This complex is of further interest since it can react with water not only by hydrolytic cleavage of the C_5Me_5 ligands but also by Sm(II) reduction.[8,9] Hence the system provided the opportunity to compare the rate of these competing reactions.

Results and Discussion

Although it has been known for many years that $(C_5Me_5)_2Sm(THF)_2$ reacts with water,[10] the product of this reaction has been difficult to identify. We now report that the main product of the reaction is a hexametallic hydroxide oxide complex. This result adds to the growing list of polymetallic organolanthanide structures that have recently been reported in the literature[11] and also correlates well with the octametallic yttrium system, $Y_8O_4Cl_{18}Li_2(THF)_{12}$, identified from an YCl_3/RLi alkylation system upon hydrolysis.[12]

The vapor over a solution of 4.5 μL of water in 5 mL of THF in one side of an H-shaped reaction vessel reacts in the other side of the H-tube with a THF solution of $(C_5Me_5)_2Sm(THF)_2$ under nitrogen to slowly produce brown crystals of **1**. By this method, **1** could be isolated directly in a crystalline form suitable for characterization by X-ray crystallography. Complex **1** has a strong IR absorption at 3636 cm^{-1}, which can be attributed to an OH stretch, but it is not soluble enough in THF to obtain an NMR spectrum. It was identified by X-ray diffraction as $[(C_5Me_5)Sm]_6O_9H_6$, **1**, Figure 1.[13]

The complex does not have pure octahedral symmetry, although the six samarium atoms roughly describe an octahedron built around a central oxygen. Eight face-bridging oxygen atoms are located in a roughly cubic array. The octahedral distortion is such that there is an elongation along the Sm(3)−Sm(3′) vector. The Sm(1) and Sm(2) bond lengths and angles are not identical, but they are equivalent within the error limits.

The Sm(3) sites have not only longer Sm−O distances to the four μ_3-oxygen atoms [2.499(4)−2.504(4) Å vs 2.407(5)−2.420(5) Å for Sm(1) and Sm(2), respectively] but also longer bond lengths to the central oxygen atom [Sm(3), 2.6086(4) Å; Sm(2), 2.485(4) Å; Sm(1), 2.477(4) Å]. The middle of the complex is more compact, with shorter O···O distances between the two sets of four oxygen atoms bound to Sm(3) and Sm(3′) than within each set of four: O(4)···O(4′), O(2)···O(5), O(3)···O(3′), and O(2′)···O(5A) are 3.134(4)−3.159(5) Å, whereas

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(13) **1** crystallizes as a THF solvate in the space group *C*2/*c* with a = 19.7076(10) Å, b = 19.3627(10) Å, c = 18.1453(9) Å. α = 90°, β = 93.0800(10)°, γ = 90°, V = 6914.1(6) Å^3, and ρ_{cacld} = 1.859 Mg/m^3 at 158 K. At convergence, wR2 = 0.0940 and GOF = 1.260 for 363 variables refined against 8233 unique data. As a comparison for refinement on F, R1 = 0.0502 for those 7180 data with $I > 2.0\sigma(I)$.

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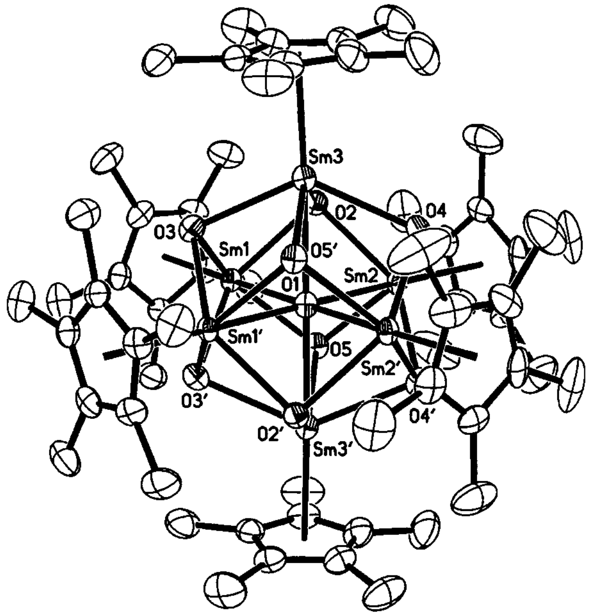

Figure 1. ORTEP drawing of $[(C_5Me_5)Sm]_6O_9H_6$, **1**. Bond angles (deg): centroid(1)−Sm(1)−O(1), 179.0; centroid(2)−Sm(2)−O(1), 178.9; centroid(3)−Sm(3)−O(1), 177.6; Sm(1)−O(1)−Sm(2′), 179.59(18); Sm(3)−O(1)−Sm(3′), 179.8(3); Sm(1′)−O(3)−Sm(3), 94.31(15), Sm(1′)−O(3)−Sm(1), 93.58(16); Sm(1)−O(3)−Sm(3), 93.69(15).

O(2)···O(3), O(3)···O(5′), O(5′)···O(4), and O(4)···O(2) are 3.210(4)−3.237(5) Å.

The Sm−C(C_5Me_5) average distances, which are equivalent within the error limits [Sm(3), 2.77(1) Å; Sm(2), 2.73(1) Å; Sm(1), 2.723(8) Å], are consistent with the presence of Sm(III)[14] and are similar to the 2.679(4) Å average in $[(C_5Me_5)Sm]_6Se_{11}$.[15] The Sm−O distances in **1** are in the range of the trivalent Sm−O(OH) distances in $\{[(Me_3Si)_2C_5H_3]_2Sm(\mu\text{-}OH)\}_2$[16] (2.40(2) Å), although these data are not very precise. Neither the crystallographic data nor the symmetry of the distortions from octahedral revealed the location of the six protons that must be present for charge balance and to account for the OH stretch in the infrared spectrum. The O···O distances are in the range of O- -H- -O hydrogen-bonded systems.[17−20]

The composition of **1** indicates that the net reaction of water with $(C_5Me_5)_2Sm(THF)_2$ occurs by both hydrolytic cleavage of one C_5Me_5 ligand and Sm(II) reduction of water. The result is a mono(cyclopentadienyl)Sm(III) fragment, a structural unit that seems to favor assembly of polymetallic compounds.[6] Such structures have recently been reviewed, and the hexametallic examples include $[(C_5Me_5)Sm]_6Se_{11}$, **2**, $\{[C_5Me_4(SiMe_2{}^tBu)]_6Yb_6I_8\}\{Li(THF)_4\}_2$,[21] **3**, and $\{[(C_5H_5)_6Yb]_6Cl_{13}\}^-$,[22] **4**. The internal structure of **2** is difficult to compare with **1** since **2** contains $(Se_2)^{2-}$ and $(Se_3)^{4-}$ components, but the relationship to the other hexametallic compounds can readily be seen. The orientation of the eight triply bridging oxygen atoms and six $[(C_5R_5)Ln]^{2+}$ units in **1** matches the positions of the eight iodides and the six $(C_5R_5)Ln$ units in **3**. Complex **1** has a central atom like **4**, although it is oxide rather than chloride. In both **1** and **4**, the distances between the metal and the central atom are longer than those between the metal and the bridging donor atoms. The peripheral 12 chlorides in **4** are edge-bridging rather than face-bridging, and this makes **4** and **1** related as are $[M_6X_{12}]_n^+$ and $[M_6X_8]_n^+$ clusters,[23] such as $[Nb_6Cl_{12}]^{2+}$ and $[Mo_6Cl_8]^{4+}$, respectively.

Since oxide and hydroxide ligands are excellent building blocks for polymetallic species,[24] the reactions of water with organometallic compounds have a significant probability of forming polymetallic products.[25] Given the numerous stoichiometric and structural variations possible in polymetallic systems, multiple products can readily form in these reactions. This may complicate isolation and identification. Hence, reactions in which partial hydrolysis has occurred may have many more reactive sites than expected based on the simple concept of "M−OH" as the hydrolysis product.

Experimental Section

The preparation of $(C_5Me_5)_2Sm(THF)_2$[26] and methods for drying solvents and taking physical measurements have been described previously.[27] Infrared analysis was carried out on a Perkin-Elmer 1600 series FTIR spectrometer. Elemental analysis was preformed by Desert Analytics, Tucson, AZ.

$[(C_5Me_5)Sm]_6O_9H_6$. A solution of $(C_5Me_5)_2Sm(THF)_2$ (140 mg, 0.248 mmol) dissolved in 10 mL of THF was added to one side of an H-shaped tube equipped with high-vacuum stopcocks on each side and a frit in the tube connecting the two sides. A degassed solution of 4.5 μL of H_2O in 5 mL of THF was added to the other side. Both solutions were degassed by the freeze−pump−thaw method. The reaction was sealed, and hydrolysis was allowed to occur over two weeks. Brown, THF-insoluble crystals of **1** (33 mg, 40%) were isolated by filtration. IR (KBr): 3636 s, 2909 s, 1440s, 1059 s, 903 m, 801w cm^{-1}. Anal. Calcd for $C_{64}H_{98}O_{10}Sm_6$: Sm, 46.76; C, 39.83; H, 5.12. Found: Sm, 46.44; C, 39.55; H, 5.26.

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Supporting Information Available: Tables of crystal data, positional parameters, bond distances and angles, and thermal parameters. The material is available free of charge via the Internet at http://pubs.acs.org.

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