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Dithionite and sulfinato complexes from the reaction of SO₂ with decamethylsamarocene†

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The reaction of $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Sm}(\text{THF})_2]$ with SO₂ resulted in four different products. The dimeric samarium complex $\{[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Sm}(\text{C}_5\text{Me}_5\text{SO}_2)]_2\}$ (**1**) crystallized from the reaction mixture first. The dithionite–sulfinato complex $\{[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Sm}(\text{S}_2\text{O}_4)]_2\{[(\eta^5\text{-C}_5\text{Me}_5)\text{Sm}(\text{C}_5\text{Me}_5\text{SO}_2)]_2\}$ (**2**), was obtained as the second major product after workup of the filtrate. Additionally, the dithionite complex $\{[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Sm}]_2(\text{S}_2\text{O}_4)\}$ (**3**) and the sulfinato complex $\{[(\eta^5\text{-C}_5\text{Me}_5)\text{Sm}]_2(\text{C}_5\text{Me}_5\text{SO}_2)_4\}$ (**4**) were isolated as minor products. All compounds were characterized by single crystal X-ray diffraction. As major reaction pathways, the reductive coupling of two SO₂ molecules to form the dithionite anion S₂O₄^{2−} and the nucleophilic attack of one samarocene C₅Me₅ ligand on the sulfur atom of SO₂ were observed.

Introduction

In terms of quantity, sulfur dioxide is one of the most industrially important chemicals. For example, it is used in the production of sulfuric acid.¹ Industrially, sulfur dioxide is produced by combustion of elemental sulfur or by oxidation of metal sulfides.¹ Besides the synthesis of sulfur-containing chemicals such as sulfuric acid, sulfur dioxide is a well-established ligand in coordination chemistry.^{2–4} The vast majority of reported compounds are based on electron-rich transition metals.^{2–5}

Besides the oxidation of sulfur dioxide to sulfur trioxide for the production of sulfuric acid,⁶ the reduction of sulfur dioxide to elemental sulfur (Claus process)⁷ or to sodium dithionite⁸ are also well-established industrial processes. In contrast to the coordination chemistry of sulfur dioxide, only a few structurally characterized dithionite complexes are known. With the exception of sodium dithionite^{9,10} $[\text{ZnS}_2\text{O}_4(\text{pyridine})]_n$,¹¹ and $[\text{Sn}_2(\text{S}_2\text{O}_4)_2]$,¹² only two families of structurally characterized dithionite transition metal complexes have been reported,

namely $[\{\text{Rh}(\text{C}_5\text{H}_4\text{R})\}_2(\mu\text{-CH}_2)_2(\mu\text{-O}_2\text{SSO}_2)]$ (R = Me, Ph, Et, nPr, CH₂Ph),^{13–18} and $\{[(\eta^5\text{-C}_5\text{Me}_5)\text{Mo}(\text{CO})_3]_2(\text{S}_2\text{O}_4)\}$.¹⁹ In both groups of complexes the dithionite ligands coordinate to the metal centers through the sulfur atoms. Today, there is growing interest in the reduction of SO₂, e.g. in main group chemistry the reduction of SO₂ with either $[(\text{THF})\text{MgNPh}]_6$ ²⁰ or $(\text{Sn}n\text{tBu})_4$,²¹ and the reactions of SO₂ with germylene²² and silylene in the gas phase have also been studied.²³ Also the reduction of SO₂ with low valent nickel compounds resulting in a thiosulfate nickel(II) compound²⁴ and the activation of SO₂ by a Cr–Cr quintuple bond²⁵ have been reported recently.

We reported on lanthanide coordination complexes that reversibly bind gaseous SO₂ at room temperature and also investigated the reduction of SO₂ with some f-element compounds.²⁶ In this context, the first sulfite $\{[(\text{P}^{\text{Me}}\text{ArO})_3\text{tacn}]\text{U}^{\text{IV}}\}_2(\mu\text{-}\kappa^1\text{-}\kappa^2\text{-SO}_3)]$ (tacn = triazacyclononane) and dithionite $\{[(\text{P}^{\text{Me}}\text{ArO})_3\text{tacn}]\text{U}^{\text{IV}}\}_2(\mu\text{-}\kappa^2\text{-}\kappa^2\text{-S}_2\text{O}_4)]$ complexes of uranium from reactions with gaseous SO₂ were reported by us.²⁷ In lanthanide chemistry we recently communicated the reaction of decamethylterbocene $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Yb}(\text{THF})_2]$ with SO₂ at low temperature, which resulted in the Yb(III) dithionite–sulfinato complex $\{[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Yb}(\text{S}_2\text{O}_4)]_2\{[(\eta^5\text{-C}_5\text{Me}_5)\text{Yb}(\text{C}_5\text{Me}_5\text{SO}_2)]_2\}$ (**A**) and the Yb(III) dithionite complex $\{[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Yb}]_2(\text{S}_2\text{O}_4)\}$ (**B**) (Scheme 1).²⁸ At elevated temperature the dinuclear tetrasulfinate complex $\{[(\eta^5\text{-C}_5\text{Me}_5)\text{Yb}]_2(\text{C}_5\text{Me}_5\text{SO}_2)_4\}$ (**C**) was obtained. In contrast, from the reaction of $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Eu}(\text{THF})_2]$ with SO₂ only the tetrasulfinate complex $\{[(\eta^5\text{-C}_5\text{Me}_5)\text{Eu}]_2(\text{C}_5\text{Me}_5\text{SO}_2)_4\}$ (**C**) was isolated (Scheme 1).

Inspired by these findings, we investigated the reaction of samarocene $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Sm}(\text{THF})_2]$ ²⁹ with SO₂. Four different complexes have been obtained, which are reported here.

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Scheme 1 Products from the reaction of $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Ln}(\text{THF})_2]$ ($\text{Ln} = \text{Eu}, \text{Yb}$) and SO_2 .

Results and discussion

Exposure of $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Sm}(\text{THF})_2]$ to SO_2 at -50°C resulted in an immediate color change from dark violet to yellow. After storing the solution overnight without stirring, single crystals of the dimeric samarium complex $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Sm}(\text{C}_5\text{Me}_5\text{SO}_2)]_2$ (**1**) suitable for X-ray diffraction formed (Scheme 2) for magnetic data of **1**, see the ESI.† The Cp^*SO_2^- ligand is formed by a nucleophilic attack of one samarocene C_5Me_5 ligand on the sulfur atom of SO_2 . As can be seen from Scheme 2 reaction products with only one Cp^* ring coordinate to the samarium atom are formed as byproducts (compounds **2** and **4**). This supports the assumption of a Cp^{*-} transfer. Compound **1**, which crystallizes in the triclinic space group $P\bar{1}$ with one molecule in the unit cell, is a dimeric Sm complex in which the two $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Sm}]^+$ units are bridged by two $\text{C}_5\text{Me}_5\text{SO}_2^-$ anions (Fig. 1). Compound **1** forms an eight-membered central ring consisting of two Sm atoms and two O–S–O units. A crystallographic

Fig. 1 Solid-state structure of **1**. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å], angles [°]: Sm–O1 2.339(2), Sm–O2' 2.355(2), S–O1 1.529(2), S–O2 1.526(2), O1–Sm–O2' 87.85(7), O1–S–O2 107.24(11).

inversion center is observed in the center of this ring. The S–O bond distances of S–O1 1.529(2) Å and S–O2 1.526(2) Å are as expected. Although we have isolated numerous products upon the reaction of SO_2 with $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Ln}(\text{THF})_2]$ ($\text{Ln} = \text{Eu}, \text{Yb}$), a compound similar to **1** has not been reported. Since the samarium ions in **1** are in the trivalent oxidation state, the samarium atoms must have been oxidized during the reaction. On the other hand, the formation of the $\text{C}_5\text{Me}_5\text{SO}_2^-$ anions is not a result of a reduction but rather of nucleophilic attack of a C_5Me_5^- group on SO_2 . This clearly indicates that other products must have been formed during the reaction.

To get a better insight into the formation of **1** the remaining filtrate was evaporated to dryness. The residue was washed with *n*-pentane giving a non-soluble residue and a yellow *n*-pentane solution. The residue was recrystallized from toluene to give yellow single crystals of the dithionite–sulfinate complex $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Sm}(\text{S}_2\text{O}_4)]_2[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Sm}(\text{C}_5\text{Me}_5\text{SO}_2)]_2$ (**2**) (Scheme 2). Another crop of crystals was collected from the remaining *n*-pentane solution. Besides complex **2**, crystals of the dithionite complex $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Sm}]_2(\text{S}_2\text{O}_4)$ (**3**) and the sulfinate complex $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Sm}]_2(\text{C}_5\text{Me}_5\text{SO}_2)_4$ (**4**) were obtained as minor products from this solution (Scheme 2). Although compounds **3** and **4** were synthesized reproducibly, we could not separate bulk products of them from mixtures with **2**. Thus, they are considered as minor products, which are not fully characterized. However, we have included these compounds to understand the reactivity of $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Sm}(\text{THF})_2]$ with SO_2 and to have a comparison to the reactions of SO_2 with $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Ln}(\text{THF})_2]$ ($\text{Ln} = \text{Eu}, \text{Yb}$).²⁸

Compound **2** is similar to **A**, which is one of the major products from the reaction of SO_2 with $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Yb}(\text{THF})_2]$.²⁸ The dithionite compound **3**, which is the analogue of **B**, was also obtained only as minor product. In contrast to **C**, which was isolated as the minor product from the reaction of SO_2 with $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Yb}(\text{THF})_2]$ at elevated temperature and as the only product from the reaction of SO_2 with $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Eu}(\text{THF})_2]$, the analogous samarium sulfinate complex **4** was only obtained as a minor product. In fact **C** was the only complex which we could isolate from the reaction of europocene with SO_2 . The difference in reactivity is obviously a result of the higher

Scheme 2 Synthesis of compounds **1–4** from $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Sm}(\text{THF})_2]$ and SO_2 .

Fig. 2 Solid-state structure of **2**. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å], angles [°]: Sm1–O1 2.341(8), Sm1–O3 2.322(8), Sm2–O2 2.322(9), Sm2–O4 2.584(8), Sm2–O4' 2.502(9), Sm2–O5' 2.320(10), Sm2–O6 2.332(9), S1–S2 2.369(5), S1–O1 1.496(8), S1–O2 1.493(10), S2–O3 1.509(8), S2–O4 1.527(9), S3–O5 1.528(10), S3–O6 1.533(10); O1–Sm1–O3 70.1(3), O2–Sm2–O4 68.7(3), O2–Sm2–O4' 144.9(3), O2–Sm2–O6 83.6(3), O4–Sm2–O6 72.8(3), O4–Sm2–O4' 77.8(3), O4–Sm2'–O5 78.6(3), O4'–Sm2'–O5 73.6(3), O4'–Sm2–O6 76.7(3), O5–Sm2–O6' 141.6(3), O1–S1–O2 109.8(6), O3–S2–O4 109.1(5), O5–S3–O6 107.1(5).

reduction potential of divalent samarium in comparison to divalent europium and ytterbium.^{30,31}

Compound **2** crystallizes in the triclinic space group $P\bar{1}$ with one molecule of the complex and two molecules of toluene in the unit cell (Fig. 2). Similarly to **A**, compound **2** is a tetranuclear complex, which has a crystallographically imposed inversion center in the central Sm–O–Sm–O ring. The molecule is assembled from two metallocene $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Sm}]^+$ and two half-sandwich $[(\eta^5\text{-C}_5\text{Me}_5)\text{Sm}]^{2+}$ units, as well as two sulfinate ($\text{C}_5\text{Me}_5\text{SO}_2^-$) and two dithionite anions. Thus, besides the already mentioned compounds **A**, **B**,²⁸ and $[\{(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}^{\text{IV}}\}_2(\mu\text{-}\kappa^2\text{-S}_2\text{O}_4)]$,²⁷ **2** is a rare example of an f-element dithionite complex. Each dithionite anion coordinates in a chelating mode to one $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Sm}]^+$ and one $[(\eta^5\text{-C}_5\text{Me}_5)\text{Sm}]^{2+}$ unit (Sm1 and Sm2). Furthermore, one of the oxygen atoms (O4) from each of the $\text{S}_2\text{O}_4^{2-}$ anions bridges the two $[(\eta^5\text{-C}_5\text{Me}_5)\text{Sm}]^{2+}$ units (Sm2 and Sm2'). As already seen in **1**, two $\text{C}_5\text{Me}_5\text{SO}_2^-$ anions are also observed in **2**. These bridge the two inner samarium atoms (Sm2 and Sm2') of $[(\eta^5\text{-C}_5\text{Me}_5)\text{Sm}]^{2+}$. Sm2 is thus coordinated to five oxygen atoms (O2, O4, O4', O5', O6) and one C_5Me_5 ligand, Sm1 is coordinated by two C_5Me_5 ligands and two oxygen atoms (O1 and O3).

Compound **3** is isostructural with one of the polymorphs of **B** and thus will not be discussed in detail. It crystallizes in the monoclinic space group $C2/c$ with one molecule in the asymmetric unit. The S–S-bridge and all C_5Me_5 ligands are disordered over two sites. Formally, **3** is formed by a redox reaction between two molecules of $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Sm}(\text{THF})_2]$ and two SO_2 molecules. Upon SO_2 reduction the central $\text{S}_2\text{O}_4^{2-}$ anion is formed, which bridges the $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Sm}]^+$ units containing trivalent samarium (Fig. 3). As observed in other dithionite complexes such as $[\text{ZnS}_2\text{O}_4(\text{pyridine})]_n$,¹¹ $[\text{Sn}_2(\text{S}_2\text{O}_4)_2]$,¹² **A**, and

Fig. 3 Solid-state structure of **3**. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å], angles [°]: Sm–O1 2.360(5), Sm–O2' 2.364(5), S1–S2 2.420(5), S1–O1 1.599(6), S1–O2 1.536(5), O1–Sm–O2 70.8(2), O1–S1–O2 104.5(3).

$[\{(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}^{\text{IV}}\}_2(\mu\text{-}\kappa^2\text{-S}_2\text{O}_4)]$,²⁷ the $\text{S}_2\text{O}_4^{2-}$ anion binds side-on to each metal atom through two oxygen atoms. The S–S axis thus lies perpendicular to the Sm–Sm axis. The S–S bond length of 2.420(5) Å is in the range of **A** (2.413(4) Å) (Fig. 3).

The cage compound **4** is similar to **C** and thus the only compound with related europium and ytterbium structures. Compound **4** crystallizes in the triclinic space group $P\bar{1}$ with one molecule of the complex and one molecule of toluene in the unit cell (Fig. 4). A crystallographic inversion center is observed in the center of the cage. As seen for **1**, a bimetallic complex is formed, in which the metal atoms are bridged by four $\text{C}_5\text{Me}_5\text{SO}_2^-$ anions *via* the oxygen atoms. In contrast to **1**, the $\text{C}_5\text{Me}_5\text{SO}_2^-$ anions do not bridge metallocene $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Sm}]^+$ units but rather half-sandwich $[(\eta^5\text{-C}_5\text{Me}_5)\text{Sm}]^{2+}$ units. Thus, for charge balance two sulfinate anions are required for each samarium atom. Each samarium atom is coordinated to four oxygen atoms and one C_5Me_5 ligand.

The oxidation state of the samarium atoms in **1** and **2** were determined by NIR (near-infrared) spectroscopy. As a result of

Fig. 4 Solid-state structure of **4**. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å], angles [°]: Sm–O1 2.331(2), Sm–O2 2.314(2), Sm–O3 2.387(2), Sm–O4 2.342(2), S1–O1 1.520(2), S1–O2' 1.529(2), S2–O3 1.536(2), S2–O4' 1.521(2); O1–Sm–O2 142.04(8), O1–Sm–O3 77.03(8), O1–Sm–O4 78.78(8), O2–Sm–O3 86.80(8), O2–Sm–O4 91.81(8), O3–Sm–O4 138.08(8), O1–S1–O2' 108.39(13), O3–S2–O4' 104.88(13).

weak ligand field splitting even in the presence of a strong visible absorption the spectra exhibited a characteristic absorbance pattern for Sm(III) complexes.^{32,33} The spectra obtained for compounds **1** and **2** show spectral patterns that are comparable to Sm³⁺/POCl₃/ZrCl₄³⁴ and Sm³⁺/SeOCl₂/SnCl₄.³⁵ The observed bands at 9224 cm⁻¹, 7773 cm⁻¹, 7294 cm⁻¹, 6821 cm⁻¹, 6455 cm⁻¹, 6384 cm⁻¹ for **1** are assigned to the transitions of the states ⁶H_{5/2} → ⁶F_{9/2}, ⁶F_{7/2}, ⁶F_{5/2}, ⁶H_{15/2} and ⁶F_{3/2} respectively. Absorption bands at 9316 cm⁻¹, 8094 cm⁻¹, 6931 cm⁻¹, 6451 cm⁻¹, 6385 cm⁻¹ for **2** can be assigned to transitions from ⁶H_{5/2} → ⁶F_{9/2}, ⁶F_{7/2}, ⁶H_{15/2} and ⁶F_{3/2}, states respectively (Fig. S1 and S2, ESI†).³⁵

Conclusions

In conclusion, we have demonstrated that the reaction of SO₂ with [(η⁵-C₅Me₅)₂Sm(THF)₂] shows some similarities to the analogous reactions with [(η⁵-C₅Me₅)₂Ln(THF)₂] (Ln = Eu, Yb). Although some related products were isolated the preferred reaction pathways are different. In addition, compound **1** represents a new class of complexes. In general, the oxidation of the divalent lanthanocenes with SO₂ proceeds *via* two major reaction pathways: (1) reductive coupling of two SO₂ molecules to form a dithionite anion S₂O₄²⁻; and (2) nucleophilic attack of one lanthanocene C₅Me₅ ligand on the sulfur atom of SO₂ forming the sulfinate C₅Me₅SO₂⁻ anionic ligand. The first reduction pathway is exclusively observed in the formation of the dithionite complex **3**, whereas the second pathway led to the formation of the metallocene compound **1** and the half-sandwich sulfinate complex **4**. Complex **2** unifies all structural building blocks from compounds **1**, **3** and **4**. Thus, in **2**, the metallocene [(η⁵-C₅Me₅)₂Sm]⁺ and half-sandwich [(η⁵-C₅Me₅)Sm]²⁺ units are bridged by dithionite S₂O₄²⁻ and sulfinate C₅Me₅SO₂⁻ anions.

Experimental section

General considerations

All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flame-dried Schlenk-type glassware either on a dual manifold Schlenk line interfaced to a high vacuum (10⁻³ torr) line, or in an argon-filled MBraun glovebox. Elemental analyses were carried out with an Elementar Vario Micro Cube. Hydrocarbon solvents were predried by using an MBraun solvent purification system (SPS-800) and degassed, dried and stored *in vacuo* over LiAlH₄. Predried tetrahydrofuran was distilled under nitrogen from K/benzophenone ketyl before storage over LiAlH₄. IR spectra were obtained on an FTIR spectrometer Bruker Tensor 37 equipped with a room temperature DLATGS detector and a diamond ATR (attenuated total reflection) unit; for the mid infrared region a KBr beamsplitter and for the far infrared region a silicon beamsplitter was used. Raman spectra were recorded on a Bruker MultiRAM spectrometer. [(η⁵-C₅Me₅)₂Sm(THF)₂]²⁹ was prepared according to a literature procedure. Magnetization data of micro-crystalline and powdered samples (10–20 mg) were

recorded with a SQUID magnetometer (Quantum Design) at 1 T in a temperature range from 2 to 300 K. Values of the magnetic susceptibility were corrected for the underlying diamagnetic increment by using tabulated Pascal constants and the effect of the blank sample holders (gelatin capsule/straw).

Synthesis of 1–4. SO₂ (0.3 mmol) was condensed onto a solution of [(η⁵-C₅Me₅)₂Sm(THF)₂] (170 mg; 0.3 mmol) in 20 ml of THF at –50 °C with stirring. The reaction mixture turned yellow immediately. The resulting solution was stirred for 1 h at –50 °C and stored overnight without stirring. Orange crystals of **1** suitable for X-ray diffraction formed and were collected by filtration (46 mg, 25%). Then, THF was removed from the filtrate by evaporation *in vacuo*. The residue was washed with 15 ml of *n*-pentane to give a non-soluble residue and a yellow *n*-pentane solution. The residue was recrystallized from toluene (10 ml) and yellow crystals of 2-2(C₆H₅CH₃) (15 mg, 9%) suitable for X-ray diffraction were collected. Storage of the *n*-pentane solution for 1 week gave a mixture of crystals of complexes **2**, and **3** (yellow crystals) and **4** (yellow crystals) as minor products, which were separated by hand.

1: IR (ATR): ν = 2980(m), 2941(m), 2912(m), 2899(m), 2858(m), 2725(w), 1437(m), 1379(w), 1357(w), 1063(w), 1024(w), 978(s), 937(s), 810(w), 694(w), 673(w), 642(w), 617(w), 600(w), 555(w), 521(m), 478(m), 409(w) cm⁻¹. NIR (ATR): ν = 9298(w), 9224(vs), 9166(vw), 9089(m), 8931(m), 8871(w), 8757(w), 8139(m), 8105(s), 8055(s), 8009(m), 7904(m), 7773(vs), 7586(vw), 7541(vw), 7294(vs), 7174(w), 7063(w), 6939(vw), 6821(vs), 6687(m), 6584(m), 6455(s), 6384(m), 6142(m) cm⁻¹. Raman (solid): ν = 2979(s), 2914(vs), 2859(vs), 2725(w), 1590(s), 1455(m), 1424(s), 1385(m), 1267(vw), 1149(vw), 1057(m), 955(s), 912(w), 804(m), 686(s), 616(m), 599(s), 554(m), 521(w), 492(m), 407(w), 383(s), 342(w), 297(s) cm⁻¹. Elemental analysis calcd (%) for C₆₀H₉₀S₂O₄Sm₂ (1240.24): C 58.11, H 7.31, S 5.17; found C 58.14, H 7.35, S 5.03.

2: IR (ATR): ν = 3475(br. m), 2966(m), 2916(m), 2858(m), 2742(w), 1444(m), 1381(m), 1319(w), 1248(w), 1211(w), 1149(w), 1064(s), 1028(s), 978(s), 962(s), 934(s), 876(s), 808(w), 642(w), 617(w), 550(w), 517(m), 494(m), 472(w), 428(w), 411(w) cm⁻¹. NIR (ATR): ν = 9316(s), 9223(m), 9157(w), 9097(m), 8811(w), 8250(m), 8192(m), 8094(vs), 8009(w), 7907(m), 7769(s), 7391(s), 7299(s), 7171(w), 7055(w), 6931(s), 6823(m), 6743(w), 6586(w), 6550(w), 6451(s), 6385(s), 6135(w), 6102(w) cm⁻¹. Raman (solid): ν = 2908(vs), 2859(s), 2725(w), 2329(w), 1592(m), 1532(vw), 1452(m), 1425(s), 1386(m), 1258(vw), 1142(w), 1067(s), 1026(s), 988(w), 938(w), 881(vw), 804(w), 698(m), 614(m), 593(s), 552(m), 518(vw), 497(vw), 406(m), 389(m), 365(w), 313(m), 283(s) cm⁻¹. Elemental analysis calcd (%) for C₈₇H₁₂₈O₁₂S₆Sm₄ = 2-toluene (2159.84): C 48.38, H 5.97, S 8.91; found C 48.52, H 6.08, S 8.73.

X-ray crystallographic studies of 1–4. A suitable crystal was covered with mineral oil (Aldrich) and mounted on a glass fiber. The crystal was transferred directly to a cold stream of a Stoe IPDS 2 or Stoe STADI-VARI diffractometer.

All structures were solved by using SHELXS-2013.³⁶ The remaining non-hydrogen atoms were located from difference in Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques on *F*, minimizing

the function $(F_o - F_c)^2$, where the weight is defined as $4F_o^2/2(F_o^2)$ and F_o and F_c are the observed and calculated structure factor amplitudes using the program SHELXL-2013.³⁶ Carbon-bonded hydrogen atom positions were calculated. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities in each case were of no chemical significance. Positional parameters, hydrogen atom parameters, thermal parameters, bond lengths and angles have been deposited as ESI.†

Crystal data for 1: $C_{60}H_{90}O_4S_2Sm_2$, $M = 1240.13$, $a = 10.5471(5)$ Å, $b = 11.2905(6)$ Å, $c = 13.1499(6)$ Å, $\alpha = 71.518(4)^\circ$, $\beta = 69.935(4)^\circ$, $\gamma = 87.015(4)^\circ$, $V = 1392.18(13)$ Å³, $T = 100(2)$ K, space group $P\bar{1}$, $Z = 1$, $\mu(MoK\alpha) = 2.21$ mm⁻¹, 11 703 reflections measured, 5444 independent reflections ($R_{int} = 0.0280$). The final R_1 values were 0.0242 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.0579 (all data). The goodness of fit on F^2 was 0.986.

Crystal data for 2: $C_{80}H_{120}O_{12}S_6Sm_4 \cdot 2(C_7H_8)$, $M = 2251.78$, $a = 12.415(2)$ Å, $b = 12.471(3)$ Å, $c = 17.870(3)$ Å, $\alpha = 97.595(16)^\circ$, $\beta = 101.297(15)^\circ$, $\gamma = 112.448(15)^\circ$, $V = 2441.3(9)$ Å³, $T = 100$ K, space group $P\bar{1}$, $Z = 1$, $\mu(MoK\alpha) = 2.554$ mm⁻¹, 28 810 reflections measured, 9596 independent reflections ($R_{int} = 0.1539$). The final R_1 values were 0.0867 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.2163 (all data). The goodness of fit on F^2 was 0.941.

Crystal data for 3: $C_{20}H_{30}O_2SSm$, $M = 484.85$, $a = 8.5615(3)$ Å, $b = 20.6022(9)$ Å, $c = 11.7388(6)$ Å, $\beta = 100.794(4)^\circ$, $V = 2033.92(16)$ Å³, $T = 100(2)$ K, space group $P2_1/n$, $Z = 4$, $\mu(MoK\alpha) = 2.998$ mm⁻¹, 9662 reflections measured, 3985 independent reflections ($R_{int} = 0.0357$). The final R_1 values were 0.0466 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.1272 (all data). The goodness of fit on F^2 was 1.044.

Crystal data for 4: $C_{60}H_{90}O_8S_4Sm_2 \cdot C_7H_8$, $M = 1460.39$, $a = 11.8154(4)$ Å, $b = 12.3472(4)$ Å, $c = 12.4497(4)$ Å, $\alpha = 76.608(2)^\circ$, $\beta = 72.242(2)^\circ$, $\gamma = 74.217(2)^\circ$, $V = 1642.46(10)$ Å³, $T = 100$ K, space group $P\bar{1}$, $Z = 1$, $\mu(MoK\alpha) = 1.949$ mm⁻¹, 17 852 reflections measured, 6440 independent reflections ($R_{int} = 0.0379$). The final R_1 values were 0.0302 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.0825 (all data). The goodness of fit on F^2 was 1.094. CCDC 1047587–1047590.

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