Reversible SO_2 Coordination

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Catching Gaseous SO_2 in Cone-Type Lanthanide Complexes: An Unexpected Coordination Mode for SO_2 in f-Element Chemistry**

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Sulfur dioxide from natural and anthropogenic emissions is thought to have a significant influence on the climate[1] and is known for the production of smog and/or acid rain.[2] Thus, the detection of SO_2 with a suitable sensor is desirable.[3] It is established that sulfur dioxide can act as a ligand in coordination chemistry[4] and the first sulfur dioxide complexes of ruthenium were reported in 1938.[5] In the last decades, a significant number of transition-metal complexes of SO_2 were synthesized[4a,b] and their structures and reactivities investigated in detail. The vast majority of these compounds are based on electron-rich transition metals.[4,6] In this context, the reversible coordination of SO_2 to platinum and nickel,[7] and in particular the use of certain platinum complexes as sensors for SO_2, were reported.[3,8] Although a broad variety of coordination modes of SO_2 are known, it typically coordinates to electron-rich transition metals either in a η^1-S coordination or in a η^2-S,O coordination mode.[6] In contrast, SO_2 preferentially binds to Lewis acids, such as *trans*-$[Mn(OPPh_3)_4(SO_2)_2]I_2$, in a η^1-O fashion.[9] In rare-earth-metal chemistry the polymeric compounds $[\{[M(SO_2)_n](AsF_6)_3\}_m]$ (M = Y, La, Ce, Pr, Nd, Sm, Gd, Dy, Er, Yb) are to our knowledge the only class of SO_2 compounds.[4c,10] As observed for other Lewis acids, the SO_2 ligand in these compounds coordinates through the O atom in η^1-fashion to the metal center. Currently no discrete molecular SO_2 complex of f-group elements is known.

Herein, we report on lanthanide coordination complexes that reversibly bind gaseous SO_2 at room temperature. The established hexadentate chelating ligand 1,4,7-tris(3,5-di-*tert*-butyl-2-hydroxybenzyl)-1,4,7-triazacyclononane ((^{tBu}ArOH)$_3$tacn), was employed,[11] which has been used extensively in uranium coordination chemistry.[12] It was shown that low-valent uranium(III) complexes, ligated by $\{(^{R}ArO)_3tacn\}^{3-}$ (R = *t*Bu, adamantyl), activate small molecules, such as CO and CO_2.[13] We were interested to explore the reactivity of the related trivalent lanthanide complexes $[\{(^{tBu}ArO)_3tacn\}Ln]$. In contrast to U^{III} coordination compounds, trivalent lanthanide complexes are significantly more stable as a result of the smaller spatial extension of the 4f orbitals compared to the 5f orbitals.[14] Thus, a fundamentally different reactivity of the $\{(^{R}ArO)_3tacn\}^{3-}$ lanthanide complexes is expected compared to the analogous 5f compounds. Although lanthanide complexes of the $\{(^{tBu}ArO)_3tacn\}^{3-}$ ligand were unknown prior to this work, the corresponding scandium compound $[\{(^{tBu}ArO)_3tacn\}Sc]$ was reported by Wieghardt et al. in 1997.[15]

The lanthanide complexes $[\{(^{tBu}ArO)_3tacn\}Ln]$ (Ln = Sm (**1**), Eu (**2**), Lu (**3**)) were obtained by reaction of (^{tBu}ArOH)$_3$tacn with $[Ln\{N(SiHMe_2)_2\}_3(thf)_2]$ (Ln = Sm, Lu; Anwander amides)[16] and $[Eu\{N(SiMe_3)_2\}_3]$,[17] respectively (Scheme 1).

Complexes **1**–**3** were characterized in the solid state by single-crystal X-ray diffraction analysis (Supporting Information, Figure S4 and S5). The $\{(^{tBu}ArO)_3tacn\}^{3-}$ ligand effectively shields the metal center, and owing to these steric constraints no additional THF molecules coordinate in the solid state to the lanthanide(III) ion, which often prefers higher coordination numbers than six. The trianionic $\{(^{tBu}ArO)_3tacn\}^{3-}$ ligand acts as a hexadentate chelator and gives rise to a facial N_3O_3 donor set resulting in six-fold coordinate lanthanide atoms. As result of the geometry and the different charge of the donor atoms in the ligand, the Ln–N bonds are significantly longer than the Ln–O bonds. Therefore, the metal atoms are located below the trigonal plane of the three aryloxide donors. Because of the smaller ion radius of lutetium the metal atom of compound **3** is more shielded. As discussed below, this has a significant influence on the reactivity. The observed geometries of compounds **1**–**3** are in agreement with the earlier reported $[\{(^{tBu}ArO)_3tacn\}Sc]$ complex.[15]

As expected, the ^{1}H NMR spectrum of **1** shows paramagnetically shifted and broadened signals in the range 0.16–7.50 ppm, while the diamagnetic compound **3** shows well-resolved signals in the ^{1}H NMR spectrum. Owing to the rigid coordination of the ligand in compound **3** the number of magnetically equivalent protons is decreased by diastereotopic splitting resulting in six signals for the methylene groups. Thus, two AB systems ($\delta = 4.03$ and 3.14 ppm, $|^2J| = 12$ Hz) and four multiplets (at ca. $\delta = 3.01$, 2.77, 2.32, and 2.23 ppm)

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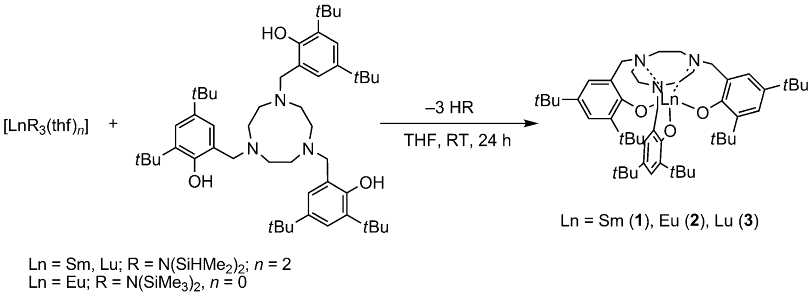
Supporting information for this article including analytical data for **2**, **3**, and **5**, is available on the WWW under http://dx.doi.org/10.1002/anie.201109109.



Scheme 1. Synthesis of **1**–**3**.

for the diastereotopic CH_2 protons of the benzyl groups and the triazacyclononane ring were observed, respectively.

In contrast to the redox-active trivalent uranium compound [{(^{tBu}ArO)$_3$tacn}U],[12] small molecules fitting into the cone-type ligand arrangement of compounds **1**–**3** are not expected to be reduced. Accordingly, treatment of compounds **1**–**3** with small molecules, such as CO and CO_2, and even pure oxygen, did not lead to a reaction, and the starting materials were recovered. Interestingly, however, the exposure of compound **1** and **2** to gaseous SO_2 at room temperature results in a spontaneous reaction as evident by an immediate color change (Figure 1). The color of the complex in solution turned from almost colorless (**1**) or yellow (**2**) to red–orange (**4**, **5**). Accordingly, a broad absorption band at 408 nm (**4**) and 398 nm (**5**) is observed in the UV/Vis spectra of **4** and **5** in solution. Performing the reactions of compounds **1** and **2** with SO_2 on a preparative scale at 0 °C results in the formation of dinuclear SO_2-bridged complexes [({(^{tBu}ArO)$_3$tacn}Ln)$_2$(μ,η^1,η^1-SO_2)] (Ln = Sm (**4**), Eu (**5**)) (see below, Scheme 2). Reaction of lutetium complex **3**, which is the complex with smallest lanthanide metal ion, does not result in formation of an SO_2 adduct. The small Lu^{III} ion in complex **3** is sterically too encumbered to provide an additional coordination site for SO_2. However, to our knowledge, complexes **4** and **5** are the first molecular lanthanide complexes with coordinated SO_2.

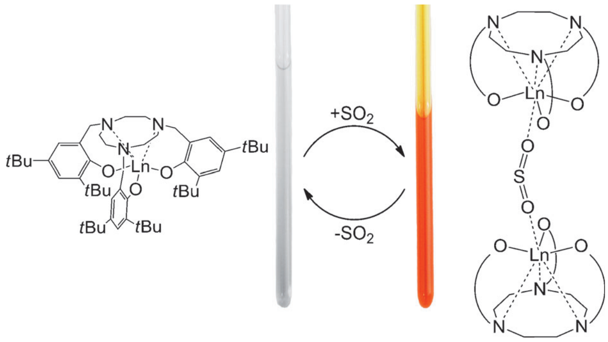
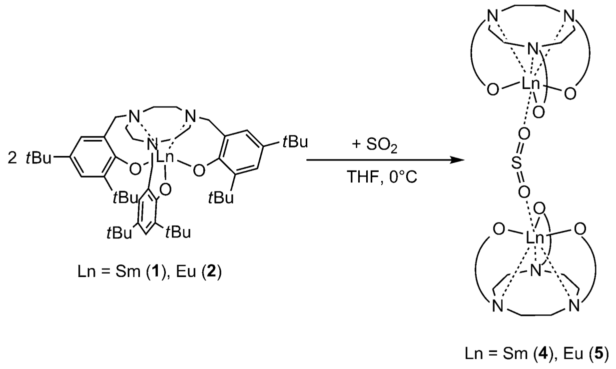


Figure 1. The reversible reaction of compound **1** with gaseous SO_2, affording **4**, results in a significant color change.

The only comparable compounds are the polymeric solid-state species [{[Ln(SO_2)$_n$](AsF_6)$_3$}$_m$] (Ln = Y, La, Ce, Pr, Nd, Sm, Gd, Dy, Er, Yb), in which the metal centers are bridged by AsF_6 units.[4c,10] In contrast to compounds **4** and **5**, these polymeric compounds could not be obtained with gaseous SO_2 but by reaction of the lanthanide metals with AsF_5 in liquid SO_2. In these polymers, the SO_2 ligands are bound in an η^1-O fashion to the metal center, and the polymers are only stable at room temperature under an atmosphere of SO_2. Complexes **4** and **5** also release SO_2 slowly at room temperature to yield starting compounds **1** and **2** showing the SO_2 coordination to be reversible.



Scheme 2. Synthesis of **4** and **5**.

Complexes **4** and **5** were fully characterized by analytical and spectroscopic methods. In addition, the solid-state structures were determined by single-crystal X-ray diffraction (Figure 2). Both compounds crystallize in the trigonal space group $R\bar{3}$. In the solid state, both compounds have a dinuclear structure, in which the metal centers are bridged by the SO_2 molecule. Thus, the SO_2 ligand is bound in a μ,η^1,η^1-O,O′ binding mode. This binding mode is rare in d- and f-block metal chemistry, with only one example known for a silver complex,[18] and is usually observed for alkaline metals, such as [$Li_2(SO_2)_8$]$^+$.[19] In contrast to **4** and **5**, all these other examples were synthesized in liquid SO_2. To the best of our knowledge a μ,η^1,η^1-coordinated SO_2 molecule has not yet been reported for the early transition metals or the f-block elements. The Ln−O2 bonds to the SO_2 molecule (2.788(6) Å (**4**) and 2.795(5) Å (**5**)) are significantly longer than in the comparable polymeric species [{[Ln(SO_2)$_n$](AsF_6)$_3$}$_m$] (e.g. 2.43(2)–2.45(1) Å in [{[Gd(SO_2)$_n$](AsF_6)$_3$}$_m$]).

Compounds **4** and **5** have an inversion center and a crystallographically imposed C_3 axis along the Ln–Ln′ axis, resulting in disordered positions for the sulfur atom (but not of the oxygen atoms).[20] Because of this disorder, the S−O bond lengths will not be discussed. In case of the Eu^{III} compounds, almost identical metric parameters for the unit cells of the precursor **2** and of the SO_2 complex **5** were found. The Eu–Eu distance in **5** (8.043(2) Å) was determined to be shorter than that in **2** (8.467(2) Å), indicating an attracting interaction of the SO_2 molecule. Nevertheless packing effects in the solid state must be considered.

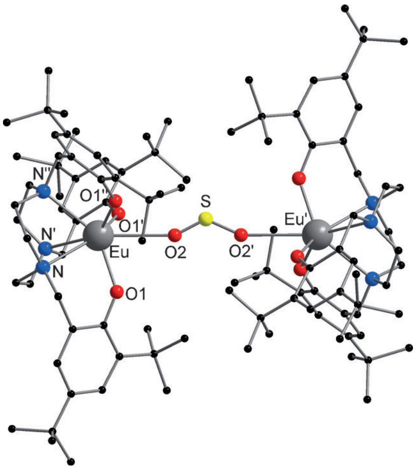


Figure 2. Solid-state structure of **5**. Hydrogen atoms, solvate molecules, and disorder of the sulfur atom are omitted for clarity. Selected bond lengths [Å] and angles [°] (data for the isostructural compound **4** are also given): **4**: Sm–O1 2.206(3), Sm–O2 2.788(6), Sm–N 2.626(4); O1-Sm-O1′ 110.93(8), O1-Sm-O2 72.03(8), O1-Sm-N 76.29(11), O1-Sm-N″ 98.25(11), O2-Sm-N 140.21(8), N-Sm-N 67.32(13), O2-S-O2 127.3(5). **5**: Eu–O1 2.199(2), Eu–O2 2.795(5), Eu–N 2.609(3); O1-Eu-O1′ 110.84(6), O1-Eu-O2 71.93(6), O1-Eu-N 76.20(9), O1-Eu-N′ 143.99(9), O1-Eu-N″ 98.12(9), O2-Eu-N 139.91(6), N-Eu-N′ 67.80(10), O2-S-O2 127.8(4).

The coordination of the SO_2 molecule is also unambiguously supported by IR and Raman data. In the IR and Raman spectra of compounds **4** and **5**, the symmetric (1328 (**4**) and 1321 cm^{-1} (**5**)) and asymmetric vibration bands (1140 (**4**) and 1137 cm^{-1} (**5**)) of the SO_2 molecule were clearly observed.[18,21]

NMR spectra of the paramagnetic complex **4** were recorded. Not surprisingly, the chemical shifts of the $\{(^{tBu}ArO)_3tacn\}^{3-}$ ligand do not differ significantly from those of compound **1**. The dinuclear nature of complex **4** in solution was further confirmed by pulsed field gradient spin-echo (PGSE) NMR spectroscopy.[22] For this purpose, PGSE NMR measurements (^1H) in $[D_8]$-THF on complexes **1** and **4** have been carried out, allowing the determination of the diffusion coefficient for **1** ($D = 5.44 \times 10^{-10}\ m^2 s^{-1}$) and **4** ($D = 4.55 \times 10^{-10}\ m^2 s^{-1}$). The data (see Supporting Information, Figures S1–S3) revealed that the hydrodynamic radius ($r_H(\mathbf{4}) = 9.7$ Å) and volume ($V_H(\mathbf{4}) = 3862$ Å^3) of complex **4** is clearly larger than for **1** ($r_H(\mathbf{1}) = 8.1$ Å; $V_H(\mathbf{1}) = 2226$ Å^3). The volume, which was roughly extracted from the X-ray structure of both complexes is ($V_{X\text{-ray}}(\mathbf{1}) = 1531$ Å^3 and $V_{X\text{-ray}}(\mathbf{4}) = 3925$ Å^3), and the corresponding radii are $r_{X\text{-ray}}(\mathbf{1}) = 7.1$ Å and $r_{X\text{-ray}}(\mathbf{4}) = 9.8$ Å. In solution the volume of compound **1** is larger than in the solid state because in solution the occupation of the vacant coordination site of the Sm^{III} atom by a THF molecule must be considered. The volume of compound **4** is in reasonable agreement with the obtained PGSE NMR data in solution. However, it must be noted that the comparison is rather crude because both X-ray structures reveal several solvent molecules in the crystal lattice, and both compounds **1** and **4** are not spherical. Nevertheless, the significant size difference of **1** and **4**, along with the different colors of compounds **1** and **4** in solution (Figure 1), indicate that the SO_2 remains coordinated to the lanthanide ion in organic solvents. In addition, these PGSE NMR measurements support the μ,η^1,η^1-O,O′ coordination of an SO_2 ligand in complexes **4** and **5**.[18,19]

Moreover, we performed density functional theory (DFT) calculations to gain further insight into the bonding of SO_2 with two equivalents of complexes **1** and **3** (see Experimental Section and Supporting Information). For computational purposes, a truncated, *ortho*-*t*Bu-substituted and trianionic ligand of 1,4,7-tris(3-*tert*-butyl-2-hydroxybenzyl)-1,4,7-triazacyclononane ($(^{tBu}ArOH)_3tacn'$) was used. To estimate the steric influence of the encumbering trianionic ligand, a comparison of a theoretical model complex $[(SmCl_3)_2(\mu,\eta^1,\eta^1\text{-}SO_2)]$, consisting of two coordinatively unsaturated $SmCl_3$ units and a bridging SO_2 molecule, with $[(\{(^{tBu}ArO)_3tacn'\}Sm)_2(\mu,\eta^1,\eta^1\text{-}SO_2)]$ (**4′**) was carried out (summary given in Table S3 of the Supporting Information). As expected from the chemical behavior of **1**, the energy of the complexation reaction [Eq. (1)] is close to zero ($\Delta E(1)$ value for $[(\{(^{tBu}ArO)_3tacn'\}Sm)_2(\mu,\eta^1,\eta^1\text{-}SO_2)]$ $+12.7\ kJ\,mol^{-1}$), whereas the reaction of $SmCl_3$ and SO_2 [Eq. (2)] is highly exothermic ($\Delta E(2)$ value for $[(SmCl_3)_2(\mu,\eta^1,\eta^1\text{-}SO_2)]$ $-146.3\ kJ\,mol^{-1}$). As found by Mulliken population analysis, the stronger bonding in the latter case is caused by a stronger charge separation within the SO_2 molecule (Q(S): +0.68 (**4′**), +0.89 ($[(SmCl_3)_2(\mu,\eta^1,\eta^1\text{-}SO_2)]$). Furthermore, this is accompanied by a shorter Sm–O bond (r(Sm–O): 267.5 (**4′**), 245.3 pm ($[(SmCl_3)_2(\mu,\eta^1,\eta^1\text{-}SO_2)]$) as well as a smaller O-S-O angle (∡(O-S-O): 114.5° (**4′**), 113.5° ($[(SmCl_3)_2(\mu,\eta^1,\eta^1\text{-}SO_2)]$).

$$2\,[\{(^{tBu}ArO)_3tacn'\}Ln] + SO_2 \rightarrow [(\{(^{tBu}ArO)_3tacn'\}Ln)_2(\mu,\eta^1,\eta^1\text{-}SO_2)] \qquad (1)$$

$$2\,SmCl_3 + SO_2 \rightarrow [(SmCl_3)_2(\mu,\eta^1,\eta^1\text{-}SO_2)] \qquad (2)$$

The weaker bonding in **4′** is caused by steric shielding of the ligand. This is in agreement with the unsuccessful synthesis of $[(\{(^{tBu}ArO)_3tacn'\}Lu)_2(\mu,\eta^1,\eta^1\text{-}SO_2)]$ with Lu^{3+} being the smallest lanthanide(III) cation. In the course of a geometry optimization calculation starting from $[(\{(^{tBu}ArO)_3tacn'\}Lu)_2(\mu,\eta^1,\eta^1\text{-}SO_2)]$, one $[\{(^{tBu}ArO)_3tacn'\}Lu]$ was removed, resulting in an unstable 1:1 complex of the composition $[\{(^{tBu}ArO)_3tacn'\}Lu(\eta^1\text{-}OSO)]$. This is in line with a strongly positive reaction energy ($\Delta E(1)$ $[(\{(^{tBu}ArO)_3tacn'\}Lu)_2(\eta^1\text{-}OSO)] = +49.7\ kJ\,mol^{-1}$). The small torsion angle of the Lu compound Φ(O-M-O-O) (122° vs. 136° in **4′**) is a criterion for the shielding by the ligand. Deviation of the ∡(O-S-O) angle of **4** and **5** compared to **4′** could be a result of the disordered S atoms in the solid-state structures of **4** and **5**.

In summary, we have prepared the first molecular SO_2 complexes of the lanthanides. They are also the first f-element compounds with a μ,η^1,η^1-O,O′-bound SO_2 molecule in the coordination sphere. In contrast to other SO_2 complexes of electron-deficient metals, the synthesis does not require liquid SO_2 but proceeds by simple treatment of the precursor compounds with gaseous SO_2 in solution. The structures of the SO_2 bridged compounds were confirmed in solution and in the solid state. Beside their unusual structural features, the compounds also have remarkable properties in solution: the uptake of gaseous SO_2 by compounds **1** and **2** is reversible, which is supported by DFT calculations, revealing a weak bonding interaction of the SO_2 ligand to the lanthanide ions. Concomitant with the addition and removal of SO_2, the color of the complexes changes between colorless and orange. Complexes **1** and **2** are remarkably stable, even in a pure oxygen atmosphere; thus, potential sensing applications will be explored.

Experimental Section

1–**3**: THF (10 mL) was condensed onto a mixture of $[\mathrm{Ln(R)_3(thf)}_n]$ (0.21 mmol; $\mathrm{R{=}N(SiHMe_2)_2}$ ($n=2$), $\mathrm{N(SiMe_3)_2}$ ($n=0$)) and $(^{t\mathrm{Bu}}\mathrm{ArOH})_3\mathrm{tacn}$ (165 mg; 0.21 mmol) and the reaction mixture was stirred overnight at room temperature. The solvent was removed in vacuo and the residue was washed with *n*-pentane. The product was crystallized from a suitable solvent.

1: $[\mathrm{Sm\{N(SiHMe_2)_2\}_3(thf)_2}]$ (145 mg, 0.21 mmol), yield: 137 mg, 0.15 mmol, 70 % as colorless crystals from hot toluene solution. Crystals suitable for X-ray crystallographic studies were obtained from cold *n*-pentane solution. ^{1}H NMR (300 MHz, $[\mathrm{D_8}]$THF, 25 °C): $\delta=7.50$ (d, $^4J=2.6$ Hz, 3H, Ph), 7.21–7.08 (m, 6H, Ph, $\mathrm{NC}\mathit{H}_2\mathrm{CH_2N}$), 6.55 (d, $|^2J|=12$ Hz, 3H, $\mathrm{NC}\mathit{H}_2\mathrm{Ph}$), 3.14 (d, $|^2J|=12$ Hz, 3H, $\mathrm{NC}\mathit{H}_2\mathrm{Ph}$), 2.84–2.74 (m, 3H, $\mathrm{NC}\mathit{H}_2\mathrm{CH_2N}$), 1.85 (s, 27H, *t*Bu), 1.37 (s, 27H, *t*Bu), 0.91–0.85 (m, 3H, $\mathrm{NCH_2C}\mathit{H}_2\mathrm{N}$), 0.25–0.16 ppm (m, 3H, $\mathrm{NCH_2C}\mathit{H}_2\mathrm{N}$). ^{13}C{^{1}H} NMR (75 MHz, $[\mathrm{D_8}]$THF, 25 °C): $\delta=167.4$ (Ph), 136.2 (Ph), 135.6 (Ph), 128.1 (Ph), 125.5 (Ph), 125.2 (Ph), 65.6 ($\mathrm{N}\mathit{C}\mathrm{H_2Ph}$), 59.9 ($\mathrm{N}\mathit{C}\mathrm{H_2CH_2N}$), 47.0 ($\mathrm{NCH_2}\mathit{C}\mathrm{H_2N}$), 36.9 (*t*Bu-*C*), 34.9 (*t*Bu-*C*), 32.6 (*t*Bu-Me), 31.7 ppm (*t*Bu-Me). MS (EI, 70 eV): *m*/*z* (%) 932 ($[M]^+$, 100), 917 ($[M{-}\mathrm{CH_3}]^+$, 11), 713 ($[M{-}\mathrm{ArO}]^+$, 3), 451 (21), 412 (5), 328 (14), 223 (10), 120 (30), 91 ($[\mathrm{Bz}]^+$, 20), 77 ($[\mathrm{Ph}]^+$, 5), 57 ($[t\mathrm{Bu}]^+$, 6). IR (ATR): $\tilde{\nu}=2952$ (w), 2904 (w), 2859 (w), 1602 (w), 1469 (m), 1439 (w), 1413 (w), 1357 (w), 1342 (w), 1307 (m), 1278 (s), 1236 (m), 1202 (w), 1166 (w), 1131 (w), 1104 (m), 1061 (w), 1002 (w), 978 (w), 948 (w), 918 (w), 881 (m), 834 (m), 809 (w), 791 (w), 770 (w), 739 (s), 697 (w), 644 (w), 608 (w), 529 (s) cm^{-1}. Raman (solid): $\tilde{\nu}=3054$ (w), 2954 (s), 2904 (w), 2772 (w), 2707 (w), 1604 (m), 1464 (m), 1341 (w), 1305 (m), 1202 (m), 1135 (w), 1028 (w), 1003 (m), 922 (m), 839 (m), 804 (w), 786 (w), 608 (w), 565 (w), 542 (w), 524 (w), 434 (w), 259 (w), 200 (w), 146 (m) cm^{-1}. Elemental analysis calcd (%) for $\mathrm{C_{51}H_{78}N_3O_3Sm\cdot{}^1\!/_2C_7H_8}$ (977.62): C 66.96, H 8.45, N 4.30; found: C 66.83, H 8.39, N 4.07.

4 and **5**: Toluene (10 mL) was condensed onto $[\{(^{t\mathrm{Bu}}\mathrm{ArO})_3\mathrm{tacn}\}\mathrm{Ln}]$ (0.1 mmol). The resulting suspension was warmed to 0 °C and the flask was flooded with SO_2 gas. The reaction mixture turned red immediately. The reaction mixture was heated until all solids had dissolved. Crystals were obtained by cooling the reaction mixture to −20 °C.

4: $[\{(^{t\mathrm{Bu}}\mathrm{ArO})_3\mathrm{tacn}\}\mathrm{Sm}]$ (93 mg, 0.1 mmol), yield: 78 mg, 0.08 mmol, 78 % as red crystals. ^{1}H NMR (300 MHz, $[\mathrm{D_8}]$THF, 25 °C): $\delta=7.53$ (d, $^4J=2.6$ Hz, 3H, Ph), 7.22–7.06 (m, 6H, Ph, $\mathrm{NC}\mathit{H}_2\mathrm{CH_2N}$), 6.78 (d, $|^2J|=12$ Hz, 3H, $\mathrm{NC}\mathit{H}_2\mathrm{Ph}$), 3.17 (d, $|^2J|=12$ Hz, 3H, $\mathrm{NC}\mathit{H}_2\mathrm{Ph}$), 2.88–2.81 (m, 3H, $\mathrm{NC}\mathit{H}_2\mathrm{CH_2N}$), 1.89 (s, 27H, *t*Bu), 1.38 (s, 27H, *t*Bu), 0.85–0.81 (m, 3H, $\mathrm{NCH_2C}\mathit{H}_2\mathrm{N}$), 0.11–0.01 ppm (m, 3H, $\mathrm{NCH_2C}\mathit{H}_2\mathrm{N}$). ^{13}C{^{1}H} NMR (75 MHz, $[\mathrm{D_8}]$THF, 25 °C): $\delta=167.6$ (Ph), 136.3 (Ph), 135.6 (Ph), 126.2 (Ph), 125.6 (Ph), 125.3 (Ph), 66.9 ($\mathrm{N}\mathit{C}\mathrm{H_2Ph}$), 59.8 ($\mathrm{N}\mathit{C}\mathrm{H_2CH_2N}$), 46.9 ($\mathrm{NCH_2}\mathit{C}\mathrm{H_2N}$), 37.0 (*t*Bu-*C*), 34.9 (*t*Bu-*C*), 32.6 (*t*Bu-Me), 31.8 ppm (*t*Bu-Me). MS (EI, 70 eV): *m*/*z* (%) 932 ($[(M{-}\mathrm{SO_2})/2]^+$, 13), 917 ($[(M{-}\mathrm{SO_2})/2\text{-}\mathrm{CH_3}]^+$, 2), 713 ($[(M{-}\mathrm{SO_2})/2\text{-}\mathrm{ArO}]^+$, 1), 523 (11), 368 (20), 236 (30), 137 (28), 95 (42), 81 (82), 69 (100), 57 ($[t\mathrm{Bu}]^+$, 72). IR (ATR): $\tilde{\nu}=2953$ (s), 2865 (w), 1602 (w), 1580 (w), 1472 (s), 1440 (m), 1414 (m), 1390 (w), 1361 (m), 1328 (w, ν_s [S=O]), 1311 (m), 1282 (m), 1235 (m), 1201 (m), 1164 (w), 1134 (m), 1105 (w), 1060 (w), 1022 (w), 1000 (w), 980 (w), 946 (m), 880 (s), 835 (m), 806 (w), 772 (w), 736 (m), 647 (m), 524 (s), 463 (w), 441 (s) cm^{-1}. Raman (solid): $\tilde{\nu}=2959$ (s), 2909 (m), 2777 (w), 2710 (w), 1603 (m), 1463 (m), 1303 (m), 1203 (m), 1140 (s, ν_{as} [S=O]), 1031 (w), 1003 (w), 927 (m), 822 (m), 802 (w), 608 (w), 560 (w), 540 (w), 519 (w), 447 (w), 259 (w), 207 (w), 118 (w) cm^{-1}. UV/Vis (THF): $\lambda_{\max}$ (nm) = 408 (very broad).

The quantum chemical DFT calculations were performed using the RI-DFT module (functional BP86)[23] of the program package TURBOMOLE.[24] Due to the large size of the molecules under discussion the basis sets of all atoms were of def2-SV(P) quality.[25] Effective core potentials were chosen for Sm (51 core electrons) and Lu (28 core electrons).[26]

CCDC 854867 (**1**), 854868 (**2**), 854869 (**3**), 854870 (**4**), and 854871 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Keywords: cage compounds · coordination compounds · lanthanides · rare-earth elements · SO_2 complexes

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