

Selective O₂ oxidation of air-sensitive lanthanocene thiolates and thioether chelate†

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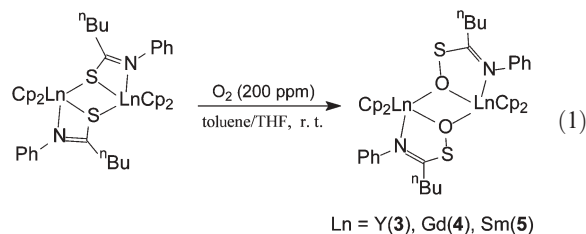
Two unusual regioselective O₂ oxidation reactions of air-sensitive lanthanocene thiolates and a thioether chelate are described, revealing a novel oxygenation pattern of thiolate ligands.

Lanthanocenes are well known but their high air-sensitivity makes controlled oxygenation difficult.¹ For example, although the O₂ oxidation decompositions of organolanthanides are frequently observed during manipulation, little is known about the structures and reactivities of initially formed reactive intermediates in these courses due to the difficulty in the control of product distribution and the isolation of the products.^{2,3} To the best of our knowledge, no example of selective oxygenation of coordinated heteroatoms has been reported in organolanthanide chemistry so far. The paucity of experiments establishing the true selectivity and the controlling method has impeded their practical applications in the selective activation of O₂.⁴

The selective oxygenation of organosulfur substrates by molecular oxygen plays a crucial role in a variety of industrial and biological processes.^{5,6} Mimic control of these oxygenations has been achieved by transition metal complexes.⁷ Although the lanthanides have a great affinity for oxygen donor ligands, this high oxophilicity disfavors the control of selective ligand-based oxygenations.⁸ Indeed, it has been uncertain whether analogous selective oxygenations of coordinated sulfur atoms also take place in the activation of O₂ by organolanthanide complexes. We report here the first selective oxygenations of lanthanide-bound thiolate and thioether, which provide the first evidence for the preferred oxygenation of coordinated sulfur atoms in lanthanocene system and reveal a novel oxygenation pattern of thiolate ligands.

Complexes {Cp₂Ln[SC(ⁿBu)NPh]}₂ [Ln = Y(**1**), Gd(**2**)] were prepared in good yields by the reaction of PhNCS with ⁿBuLi and subsequently with Cp₂LnCl in toluene. Interestingly, when a THF–toluene solution of **1** (or **2**) was exposed to an N₂ atmosphere with limited amount of dried air at ambient temperature (*ca.* 12 °C), both were converted into O-bound sulfenate complexes {Cp₂Ln[OSC(ⁿBu)NPh]}₂ [Ln = Y(**3**), 35% yield; Ln = Gd(**4**), 41% yield] with small amounts of unidentified decomposition products. The samarium analogue {Cp₂Sm[OSC(ⁿBu)NPh]}₂ (**5**) was obtained in 44% yield by the reaction of Cp₂SmCl·THF with PhNC(ⁿBu)SLi in toluene, followed by slow diffusion of trace O₂ into the reaction flask.

The formation of **3–5** may be interpreted as a single oxygen atom, from molecular oxygen, insertion into the Ln–S bond of {Cp₂Ln[SC(ⁿBu)NPh]}₂ [eqn. (1)]. Although controlled O₂ oxidation of thiolate complexes has been investigated extensively, only MS(O)₂R, MOS(O)R, MO₃SR and MS(O)R-type ligand-based oxygenation products were isolated without the observation of the MOSR-type single oxygen insertion product.⁷ Sodium thiolates do not yield the corresponding *S*-oxygenates.^{7a} This unique selectivity might be partly attributed to the difference in the oxophilicity and the thiophilicity between lanthanides and d-transition elements.



Complexes **1–5** were characterized by elemental analysis, IR and mass spectroscopy, which were in good agreement with the proposed structures. Presumably, the structures of **1** and **2** may be similar to that of [Cp₂Y(μ-η²:η¹-SC(NPh₂)NPh)]₂.⁹ The X-ray analysis shows that **3** and **5** are isomorphous,^{†,‡,§} and both are centrosymmetric dimers in which each metal ion is coordinated by two η⁵-Cp groups, two bridging oxygens, and one chelating nitrogen to form a distorted trigonal bipyramidal (Fig. 1). The S–O distance in **3** is slightly longer than the values observed in O-bound sulfinate complexes (1.51–1.56 Å).^{7b,c} This is in agreement with the expectation that the S–O distances decrease with increasing oxygenation. The bond angle of C(11)–S(1)–O(1) [103.2(2)°] indicates that the sulfur atom is sp³ hybridized. The average Y–O distance of 2.336(2) Å is compared to the Y–O distances observed usually in other dinuclear oxygen-bridging complexes, such as [Cp₂Y(μ-OH)]₂ [average 2.35(2) Å],^{10a} and [(Me₃SiC₅H₄)₂Y(μ-OMe)]₂ [average 2.225(3) Å].^{10b} The Y–N distance of 2.546(3) Å is in the normal range of observed Y←N donor bond distances (2.44–2.72 Å).¹¹ The structural parameters of **5** are very similar to those for complex **3**. All the Sm–O, Sm–N and Sm–C distances are in the ranges expected.¹²

After having established the unique selectivity of controlled O₂ oxidation of trivalent lanthanocene thiolates, we were interested to examine whether related selective O₂ oxidation was accessible on a chelating thioether group. To that purpose, (EtSCH₂CH₂C₅H₄)₃Sm (**6**) was prepared in 54% yield by the reaction of SmCl₃ with 3 equivalents of NaC₅H₄CH₂CH₂SEt in THF.¹³ Treatment of a solution of **6** in THF with trace O₂ added

† Electronic supplementary information (ESI) available: experimental procedures and characterization data for compounds **1–7**. See <http://www.rsc.org/suppdata/cc/b4/b417609j>
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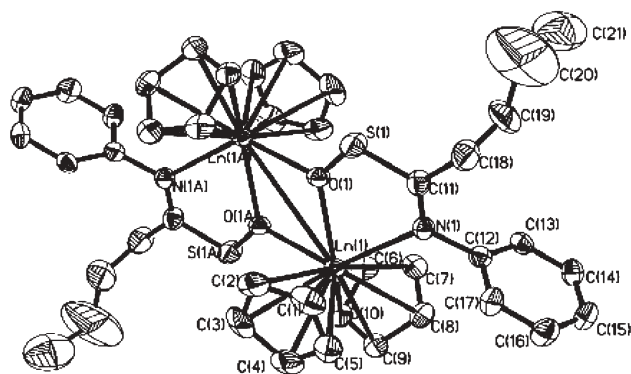


Fig. 1 ORTEP diagrams of **3** (Ln = Y) and **5** (Ln = Sm) with the probability ellipsoids drawn at the 30% level. Selected bond lengths (Å) and angles (°): for **3**: Y(1)–O(1) 2.316(2), Y(1)–O(1A) 2.357(2), Y(1)–N(1) 2.546(3), Y–C_{av} 2.67(1), S(1)–O(1) 1.596(2), S(1)–C(11) 1.712(4), N(1)–C(11) 1.272(5), N(1)–C(12) 1.446(5), O(1)–Y(1)–O(1A) 65.8(1), Y(1)–O(1)–Y(1A) 114.2(1), O(1A)–Y(1)–N(1) 130.0(1), O(1)–Y(1)–N(1) 69.1(1), O(1)–S(1)–C(11) 103.20(17). For **5**: Sm(1)–O(1) 2.394(4), Sm(1)–O(1A) 2.418(5), Sm(1)–N(1) 2.590(6), Sm–C_{av} 2.74(1), N(1)–C(11) 1.281(9), N(1)–C(16) 1.456(9), O(1)–S(1) 1.582(5), S(1)–C(11) 1.712(8), O(1)–Sm(1)–O(1A) 66.7(2), Sm(1)–O(1)–Sm(1A) 113.3(2), O(1)–Sm(1)–N(1) 67.6(2), O(1A)–Sm(1)–N(1) 131.6(2), S(1)–O(1)–Sm(1) 124.0(2), S(1)–O(1)–Sm(1A) 122.6(2), O(1)–S(1)–C(11) 103.7(3).

intermittently over several days at ambient temperature under an atmosphere of nitrogen, gave the unusual side-chain oxidation product (EtSC₂H₄C₅H₄)₂[EtS(O)C₂H₄C₅H₄]₂Sm (**7**) in 43% yield [eqn. (2)]. The crystal structure of **7** clearly demonstrates that one thioether substituent is selectively converted to the O-bound sulfoxide group in the course of controlled O₂ oxidation and the bonding model of the cyclopentadienyl ring to Sm³⁺ remains unchanged (Fig. 2). **7** represents the first sulfoxide-substituted cyclopentadienyl complex of lanthanide metals. Taking the difference of metal ionic radii into account, the Sm–O distance

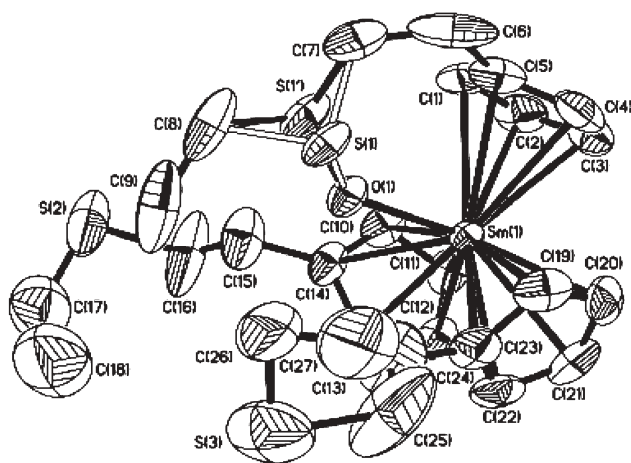
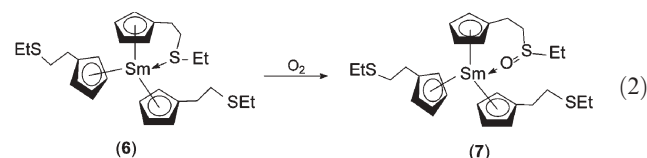


Fig. 2 ORTEP diagrams of **7** with the probability ellipsoids drawn at the 30% level. Selected bond lengths (Å) and angles (°): Sm(1)–C 2.72(1)–2.82(1), S(1)–S(1′) 1.35(2), S(1)–O(1) 1.506(6), S(1′)–O(1) 1.45(2), O(1)–S(1)–C(8) 106.8(6), O(1)–S(1)–C(7) 106.3(6), C(8)–S(1)–C(7) 94.1(9), O(1)–S(1′)–C(7) 115.9(14), O(1)–S(1′)–C(8) 104.7(18), C(7)–S(1′)–C(8) 95.0(14), C(17)–S(2)–C(16) 100.2(13), C(26)–S(3)–C(25) 97.8(12), S(1′)–O(1)–Sm(1) 128.5(12), S(1)–O(1)–Sm(1) 138.0(4).

of 2.34(1) Å is comparable with that found in sulfoxide complex (C₉H₇)₃La[OSMe(*p*-tolyl)], 2.453(5) Å,¹⁴ but is slightly shorter than the values observed in ten-coordinate carbonyl donor adducts, such as Cp₃Dy(OCPh₂) [2.38(1) Å],¹⁵ Cp₃Ln(Me₂NCONMe₂) [Ln = Ce, 2.46(1) Å; Ln = Nd, 2.44(1) Å],¹⁶ and Cp₃Pr(CH₃CO₂C₄H₉) [2.50(1) Å].¹⁷ The angles O–S–C and C–S–C are practically identical to the corresponding angles in (C₉H₇)₃La[OSMe(*p*-tolyl)], respectively.¹⁴ Attempts to obtain the products attributable to the further oxygenation of other sulfur atoms by using larger amounts of O₂ and longer reaction times were unsuccessful, giving over-oxidation to metal oxide.



For metal-based stoichiometric conversion of thioethers to sulfoxides by molecular oxygen, high oxygen concentration and the addition of reducing agents are usually required.¹⁸ It is unexpected that the present O₂ oxidation of the thioether substituent can occur at very low O₂ concentration (*ca.* 200 ppm) and at ambient temperature without any reducing equivalent. On the other hand, although the modification of the cyclopentadienyl ligand is a highly desirable transformation,¹⁹ it is generally difficult to accomplish with lanthanide complexes since such a process breaks readily the original lanthanide–ligand bond.²⁰ To our knowledge, the transformation of **6** to **7** represents the first example of the selective oxygenation of the pendent functional group on the cyclopentadienyl skeleton of lanthanide complexes in which complex integrity is retained.

Surprisingly, contrary to the general impression that oxygenations are relatively uncontrollable, and that the O₂-based oxidation readily results in degradation of trivalent lanthanocenes to metal oxides,³ the Ln–C(η⁵-Cp) bond is left unaffected in the present controlled O₂ oxidation process. The compatibility of the selective oxygenation of coordinated sulfur atoms with the Ln–Cp bond demonstrates a remarkable range of oxygenation levels, indicating that the reaction of trivalent lanthanocene derivatives with O₂ may not always lead to Ln–C bond cleavage as the preferred reaction pathway, and providing a new insight into the behavior of organolanthanides.

In conclusion, two unusual regioselective O₂ oxidation reactions of air-sensitive organolanthanides have been established, demonstrating for the first time that the coordinated thiolate and thioether sulfurs are more reactive to O₂ than the cyclopentadienyl ligand under the conditions involved and revealing a novel oxygenation pattern of the thiolate ligand. Furthermore, these observations not only demonstrate that lanthanide metals are competent for the promoted O₂ oxidation of coordinated sulfur-containing ligands, but portend that the vexing air sensitivity of organolanthanide complexes, if controlled, might prove useful in the synthesis of new organolanthanide derivatives.

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Notes and references

† Crystal data for **3**, C₄₂H₄₈N₂S₂O₂Y₂, *M* = 683.82, monoclinic, space group *P*2₁/*n*, *a* = 8.6313(12), *b* = 18.633(3), *c* = 12.9330(18) Å, β = 104.947(2)°, *V* = 2009.6(5) Å³, *Z* = 2, μ = 3.014 mm⁻¹, 10510 data collected, 4519 unique data (*R*_{int} = 0.0325), 3457 data with *I* > 2σ(*I*), *R*₁ = 0.044, *wR*₂ = 0.1056. For **5**: C₄₂H₄₈N₂S₂O₂Sm₂, *M* = 957.48, monoclinic, space group *P*2₁/*n*, *a* = 8.719(2), *b* = 18.791(5), *c* = 12.978(3) Å, β = 104.453(3)°, *V* = 2059.0(9) Å³, *Z* = 2, μ = 2.960 mm⁻¹, 9293 data collected, 4028 unique data (*R*_{int} = 0.0577), 2732 data with *I* > 2σ(*I*), *R*₁ = 0.0476, *wR*₂ = 0.0955.

§ CCDC 205595, 205596 and 208202. See <http://www.rsc.org/suppdata/cc/b4/b417609/> for crystallographic data in .cif or other electronic format.

¶ Crystal data for **7**: C₂₇H₃₉OS₃Sm, *M* = 626.11, monoclinic, space group *P*2₁/*n*, *a* = 8.716(3), *b* = 19.324(7), *c* = 17.250(6) Å, β = 100.119(5)°, *V* = 2860.4(19) Å³, *Z* = 4, μ = 2.288 mm⁻¹, 11794 data collected, 5026 unique data (*R*_{int} = 0.0398), 4039 data with *I* > 2σ(*I*), *R*₁ = 0.0649, *wR*₂ = 0.1382.

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