

Lanthanide Thiolate Complexes: Synthesis of $[\text{Ln}\{\text{N}(\text{SiMe}_3)_2\}(\mu\text{-SBut}^t)]_2$ (Ln = Eu, Gd, Y) and the X-Ray Crystal Structure of the Gd Complex

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The lanthanide thiolate complexes $[\text{LnL}_2(\mu\text{-SBut}^t)]_2$ [L = N(SiMe₃)₂; Ln = Eu, Gd, Y] have been prepared by reaction of $[\text{LnL}_2\text{Cl}(\text{THF})]_2$ (Ln = Eu, Gd; THF = tetrahydrofuran) or $\text{LnL}_2\text{Cl}(\text{THF})_2$ (Ln = Y) with LiSBut^t; the X-ray crystal structure of $[\text{GdL}_2(\mu\text{-SBut}^t)]_2$ is reported.

Trivalent lanthanides are generally considered to be 'hard' metals, most readily forming complexes with 'hard' ligands, and there is an extensive co-ordination chemistry of the lanthanides with O-donor ligands. There are fewer complexes with N-donor ligands, though the number is still considerable. Among 'soft' ligands the dithiocarbamate¹ and dithiophosphate² complexes are the only ones with S-donor ligands which have been structurally characterised. Potentiometric titrations indicated the formation of $\text{Ln}(\text{SR})_3$ in solution for Ln = La, Ce; R = furfuryl,³ and for Ln = La, Ce, Pr, Sm; R = methyl-3-mercaptopropionate.⁴ In these cases no products were isolated. Dark brown pastes have been isolated from the

reactions of tris(cyclopentadienyl)cerium(IV) chloride and bis(indenyl)cerium(IV) dichloride with thiols. These materials were formulated as $[(\eta^5\text{-C}_5\text{H}_5)_3\text{Ce}(\text{SR})]$ and $[(\eta^5\text{-C}_7\text{H}_9)_2\text{-Ce}(\text{SR})_2]$.⁵

We now report the synthesis of $[\text{LnL}_2(\mu\text{-SBut}^t)]_2$ [L = N(SiMe₃)₂; Ln = Eu, Gd, Y] and the X-ray crystal structure of the Gd complex, the first structurally characterised lanthanide thiolate complex. Reaction of $[\text{LnL}_2(\mu\text{-Cl})(\text{THF})]_2$ ⁶ (Ln = Eu, Gd) with two equivalents of LiSBut^t in tetrahydrofuran (THF) under strictly anaerobic conditions gives $[\text{LnL}_2(\mu\text{-SBut}^t)]_2$. THF is removed *in vacuo* and the residue extracted with hot toluene. Crystallisation by slow cooling of a saturated

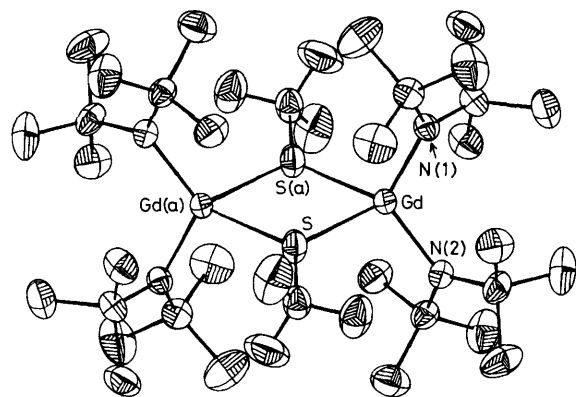


Figure 1. Molecular structure of $[\text{GdL}_2(\mu\text{-SBu}^t)]_2$. Selected bond lengths (in Å) and angles (in °) are: Gd–S 2.760(5); Gd–S(a) 2.823(5); Gd–N(1) 2.230(6); Gd–N(2) 2.244(6); S–Gd–S(a) 70.9(2); Gd–S–Gd(a) 109.1(2); N(1)–Gd–N(2) 113.6(3); S–Gd–N(1) 121.2(2); S–Gd–N(2) 105.2(2); S(a)–Gd–N(1) 105.2(2); S(a)–Gd–N(2) 135.0(1).

toluene solution gives the product in *ca.* 50% yield as well-formed prisms. The Gd complex is colourless; the Eu complex is very deep red in solution but gives crystals which are almost black. These compounds are thermally quite stable, but decompose rapidly on exposure to oxygen or moisture. The corresponding Y complex can be prepared similarly from $\text{YL}_2\text{Cl}(\text{THF})_2$ ⁶ and is colourless.

The X-ray crystal structure† of $[\text{GdL}_2(\mu\text{-SBu}^t)]_2$ is shown in

† *Crystal Data:* $\text{C}_{32}\text{H}_{90}\text{N}_4\text{S}_2\text{Si}_8\text{Gd}_2$, $M = 1133.5$, monoclinic, $a = 12.123(3)$, $b = 11.434(2)$, $c = 20.556(5)$ Å, $\beta = 91.50(2)^\circ$, space group $P2_1/n$, $Z = 2$ (dimer centrosymmetric), $D_c = 1.32$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 24.4$ cm⁻¹. Data were recorded using graphite monochromated Mo-K α radiation and a CAD4 diffractometer. Of the 5610 data recorded, 4998 were unique and 4428 were deemed observed [$I > 1.5 \sigma(I)$] and used in the analysis. Structure solution was *via* the heavy atom method and refinement was by least squares (heavy atoms anisotropic, hydrogen atoms isotropic). Final R, R' values are 0.0339 and 0.0363 respectively. Atomic co-ordinates are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

Figure 1, along with important bond lengths and angles. Microanalytical and ¹H n.m.r. data‡ for the Eu and Y complexes are consistent with their having a similar structure, although we are unable to distinguish from ¹H n.m.r. data between a monomeric and a dimeric structure in solution.

$[\text{EuL}_2(\mu\text{-SBu}^t)]_2$ has also been prepared by careful addition of one equivalent of Bu^tSH to a solution of EuL_3 in toluene–THF at –23 °C. If the addition is done at higher temperatures an insoluble orange material, presumably a $\text{Eu}(\text{SBu}^t)_3$ polymer, is formed and the only soluble material isolated is unreacted EuL_3 . YL_3 reacts less readily with Bu^tSH, probably owing to the smaller ionic radius of Y^{3+} (0.893 *cf.* 0.950 Å for Eu^{3+}). Addition of one equivalent of Bu^tSH to an Et₂O solution of YL_3 at –10 °C followed by stirring at room temperature for 2–3 hours results in the formation of $[\text{YL}_2(\mu\text{-SBu}^t)]_2$ as a white precipitate.

The soft thiolate ligand may be expected to lead to a considerable degree of covalency in the lanthanide-to-ligand bond, manifesting itself as a large zero-field splitting of the lanthanide ion ground state. In order to investigate this effect we are undertaking a single crystal e.s.r. study of the paramagnetic $[\text{GdL}_2(\mu\text{-SBu}^t)]_2$ doped into the diamagnetic Y complex.

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‡ Satisfactory analytical data were obtained. ¹H N.m.r. (CDCl_3 , room temperature): $[\text{EuL}_2(\mu\text{-SBu}^t)]_2$ δ 4.92 (s, 36H, SiMe₃), 24.08 (s, 9H, Bu^tS); $[\text{YL}_2(\mu\text{-SBu}^t)]_2$ 0.25 (s, 36H, SiMe₃), 1.65 (s, 9H, Bu^tS).