Formation of Lanthanoid(II) and Lanthanoid(III) Thiolate Complexes derived from Metals and Organic Disulfides: Crystal Structures of [{Ln(SAr)(μ-SAr)(thf)₃}₂] (Ln = Sm, Eu), [Sm(SAr)₃(py)₂(thf)] and [Yb(SAr)₃(py)₃] (Ar = 2,4,6-Triisopropylphenyl; py = Pyridine)

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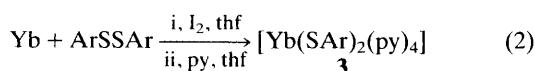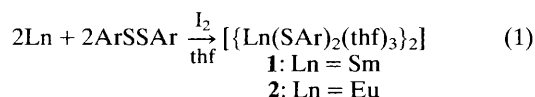[b] Department of Macromolecular Science, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan
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Reaction of metallic samarium, europium and ytterbium with bis(2,4,6-triisopropylphenyl) disulfide gave selectively Ln(II) thiolate complexes, [{Ln(SAr)(μ-SAr)(thf)₃}₂] Ln = Sm 1; Ln = Eu 2 and [Yb(SAr)₂(py)₄] 3, as well as Ln(III) thiolate complexes, [Ln(SAr)₃(py)ₙ(thf)₃₋ₙ]: Ln = Sm, n = 3 4a; Ln = Sm, n = 2 4b; Ln = Yb, n = 3 5, (Ar = 2,4,6-trisopropylphenyl) depending on the stoichiometry of the lanthanoid and the disulfide; the molecular structures of 1, 2, 4b and 5 were determined by X-ray crystallography.

Chalcogenolate complexes of lanthanoid elements are of interest both as precursors for new materials and for understanding the bonding between the lanthanoid and chalcogen.[1–7] Such complexes have been synthesised by metathesis reactions of lanthanoid halides with chalcogenolate anions.[8–12] In these reactions, the tendency to form polymeric structures with bridging chalcogenolate ligands often hinders purification. In order to prepare salt-free complexes, the reaction of bis(trimethylsilyl)amide and bis(trimethylsilyl)-methyl complexes of lanthanoids with bulky thiols[13] and the oxidative reaction of low-valent organolanthanoid complexes with organic disulfides[14–16] have been used. However, usually a mixture of Ln(II) and Ln(III) complexes results and purification by recrystallization is precluded by the instability to air and atmospheric moisture. We have now found that Ln(II) and Ln(III) arenethiolates are selectively formed by the direct reaction of the lanthanoid metal with a bulky diaryl disulfide.

Treatment of an excess of metallic samarium with bis(2,4,6-triisopropylphenyl) disulfide in thf at 50 °C for 24 h in the presence of a catalytic amount of iodine afforded a dark green solution, from which dark green prisms‡ of [{Sm(SC₆H₂Pri₃-2,4,6)₂(thf)₃}₂] 1 were obtained in 74% yield [eqn. (1)]. Similarly, [{Eu(SC₆H₂Pri₃-2,4,6)₂(thf)₃}₂] 2 was obtained as yellow crystals‡ in 56% yield. The reaction of metallic Yb and bis(2,4,6-triisopropylphenyl) disulfide in thf gave an oily orange product. When an excess of pyridine was added to the orange solution in thf, the solution became black. Recrystallization afforded [Yb(SC₆H₂Pri₃-2,4,6)₂(py)₄] 3 as black crystals‡ in 46% yield [eqn. (2)].

$$2Ln + 2ArSSAr \xrightarrow[thf]{I_2} [\{Ln(SAr)_2(thf)_3\}_2] \quad (1)$$
$$1: Ln = Sm$$
$$2: Ln = Eu$$

$$Yb + ArSSAr \xrightarrow[ii, py, thf]{i, I_2, thf} [Yb(SAr)_2(py)_4] \quad (2)$$
$$3$$

Selective formation of Sm(III) and Yb(III) thiolate complexes from the same source, the metallic lanthanoid and diaryl disulfide, has been accomplished. Metallic samarium and ytterbium reacted smoothly with 3 equiv. of bis(2,4,6-triisopropylphenyl) disulfide under the same condition. Addition of an excess of pyridine followed by filtration and concentration of the solution gave [Ln(SAr)₃(py)₃]; Ln = Sm 4a; Ln = Yb 5§ in 39 and 30% yields, respectively [eqn. (3)]. Recrystallization of 4a from thf afforded [Sm(SAr)₃(py)₂(thf)] 4b as crystals§ suitable for X-ray crystallographic study. In the case of europium, however, only a bivalent europium complex [{Eu(SAr)₂(thf)₃}₂] 2, was produced, even when >3 equiv. of the disulfide were used. This is consistent with the fact that bivalent europium complexes were prepared from the corresponding Eu(III) halide.[10]

$$Ln + 3/2ArSSAr \xrightarrow[ii, py, thf]{i, I_2, thf} [Ln(SAr)_3(py)_3] \quad (3)$$
$$4a: Ln = Sm$$
$$5: Ln = Yb$$
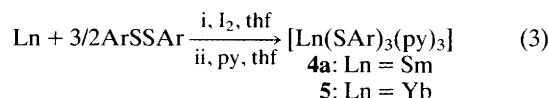
The molecular structure of compound 1 is shown in Fig. 1.¶ Compound 2¶ has essentially the same structure as 1, and selected bond distances and angles for 2 are given in the caption. Both complexes 1 and 2 have a binuclear structure with one bridging and one terminal thiolate with the molecule lying on a crystallographic centre of symmetry. The Ln₂S₂ units are planar in both complexes. The metal centres in 1 and 2 have a distorted octahedral geometry with three thiolate and three thf ligands in meridional fashion. Fig. 2 shows the molecular structure of 4b.¶ Complex 5¶ has the same structure as 4b except that a coordinated pyridine replaces the thf ligand in 4b. Complexes 4b and 5 have a distorted octahedral geometry with three thiolate ligands in meridional fashion.

The Sm–S distance [2.908(6) Å] of the terminal thiolate in 1 is longer than those of the trivalent complexes 4b [av. 2.740(3) Å], [Li(tmeda)]₃[Sm(SBuᵗ)₆] (tmeda = tetramethyl-ethylenediamine) [av. 2.827(3) Å][12] and [Sm(SC₆H₂Buᵗ₃-2,4,6)₃] [av. 2.644(8) Å].[13] The Sm–S distance [av. 3.017(5) Å] of the bridging thiolate in 1 is significantly longer by 0.136 Å
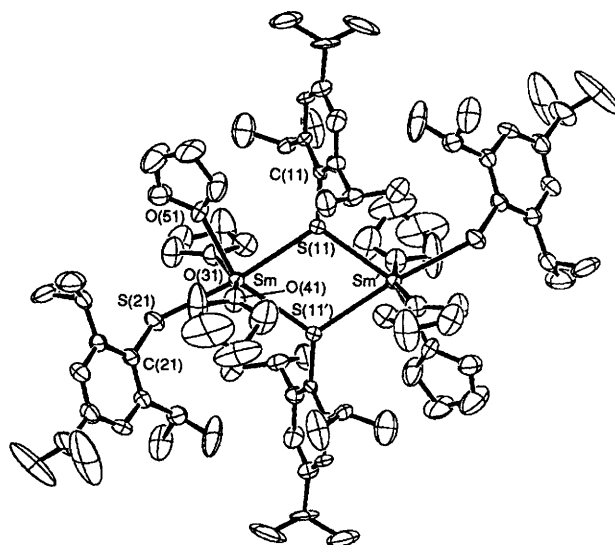
Fig. 1 A drawing of 1 with the numbering scheme. Complex 2 is isostructural. Selected bond distances (1/2, Å) and angles (1/2, °): Ln–S(11) 3.035(5)/3.030(3), Ln–S(11′) 2.999(6)/3.001(3), Ln–S(21) 2.908(6)/2.898(4), Ln–O(31) 2.62(2)/2.593(9), Ln–O(41) 2.59(2)/2.583(9), Ln–O(51) 2.62(2)/2.557(10), S(11)–Ln–S(11′) 68.8(2)/69.0(1), Ln–S(11)–Ln′ 111.2(2)/111.0(1), S(11)–Ln–S(21) 170.6(2)/170.82(9), Ln–S(11)–C(11) 124.0(6)/124.8(4), Ln′–S(11)–C(11) 123.4(7)/122.7(5), Ln–S(21)–C(21) 124.0(8)/124.6(5).
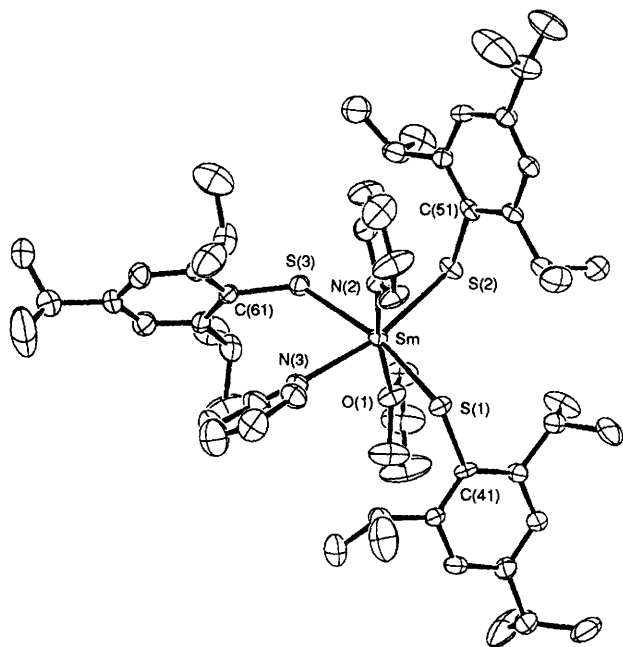
Fig. 2 A drawing of **4b** with the numbering scheme. Complex **5** is isostructural except for the partial replacement of thf by pyridine. Selected bond distances (**4b/5**, Å) and angles (**4b/5**, °): Ln–S(1) 2.751(3)/2.665(6), Ln–S(2) 2.720(3)/2.622(7), Ln–S(3) 2.749(3)/ 2.656(6), Ln–[O(1)/N(1)] 2.422(7)/2.38(2), Ln–N(2) 2.533(9)/2.42(2), Ln–N(3) 2.543(9)/2.43(2), Ln–S(1)–C(41) 122.2(3)/114.4(8), Ln–S(2)–C(51) 116.4(3)/115.6(8), Ln–S(3)–C(61) 126.9(4)/120.4(7).

than that in the trivalent samarium complex [Sm(μ-SC₆H₂Prⁱ₃-2,4,6)(η-C₈H₈)(thf)]₂ **6** [av. 2.881(5) Å].[4a] These differences in Sm–S distances can be attributed to the size of the metal ions, *i.e.* Sm^II, 1.11 Å; Sm^III, 1.00 Å, as well as the coordination geometry. Complex **2** has similar Eu–S distances to those in **1**, which is reasonable considering the similar atomic size of Eu^II and Sm^II. For complex **5**, the average Yb–S distances [2.648(7) Å] are comparable to those in the Yb^III complex having a terminal thiolate, [Yb(C₅Me₅)₂(SPh)(NH₃)] (av. 2.675(3) Å),[14a] and shorter than those of the Yb^III complex bearing thiolate ligands bridging between Yb and Li, [Li(tmeda)]₃[Yb(SBuᵗ)₆] [av. 2.737(2) Å],[12] and the bivalent complex, [Yb(SC₆H₂Buᵗ₃-2,4,6)₂(dme)₂] [2.756(8) Å].[13]

Preliminary investigations indicate that these binuclear Ln^II complexes have versatile reactivity. Reaction of **1** with 1 equiv. of cyclooctatetraene afforded **6**[4a] and [Sm(SC₆H₂Prⁱ₃-2,4,6)₃(thf)ₓ]ₙ. When **1** was treated with 2 equiv. of cyclo-octatetraene and 1 equiv. of metallic samarium, **6** was isolated as purple crystals in 69% yield. Reaction of benzyl bromide with 2 equiv. of **1** afforded bibenzyl in 58% yield.

Footnotes

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‡ The isolated crystals of these complexes gradually become opaque as they lose thf. Thus, elemental analyses of **1** and **2** are consistent with their composition as mono- and bis-thf adduct, respectively.

1: mp 160–178 °C (decomp.); **2**: mp >300 °C (decomp.); **3**: mp 170–215 °C (decomp.).

§ **4a**: mp 160–164 °C. **4b**: mp 163–167 °C. **5**: mp 198–201 °C. Elemental analyses were consistant with the formulations.

¶ *Crystal data for* **1**: C₈₄H₁₄₀O₆S₄Sm₂, M_r = 1675.06, monoclinic, space group $P2_1/c$ with a = 12.715(7), b = 20.802(4), c = 18.137(3) Å, β = 108.92(2)°, V = 4538(2) Å³, Z = 2, D_c = 1.226 g cm⁻³, 3319 reflections [$I > 3\sigma(I)$, $(2\theta_{max}$ = 55.0°, 2θ–ω scan, 23 °C] collected on a Rigaku AFC-5R diffractometer using Mo-Kα radiation. Data corrected for absorption by an azimuthal scan of a reflection having χ near 90°. Structure solved by the Patterson method and refined by full-matrix least squares (TEXSAN package) to R = 0.068, R_w = 0.079. H-atoms were located at the calculated positions and not refined. The following crystallographic studies were carried out similarly.

2: C₈₄H₁₄₀Eu₂O₆S₄, M_r = 1678.19, monoclinic, space group $P2_1/c$ with a = 12.685(5), b = 20.799(4), c = 18.130(3) Å, β = 108.88(2)°, V = 4526(1) Å³, Z = 2, D_c = 1.231 g cm⁻³, R = 0.071, R_w = 0.043 for 3777 reflections [$I > 3\sigma(I)$, 2θ_{max} = 55.0°, 2θ–ω scan, 23 °C].

4b: C₅₉H₈₇N₂OS₃Sm, M_r = 1086.93, triclinic, space group $P\bar{1}$ with a = 14.580(3), b = 18.627(4), c = 12.383(4) Å, α = 104.67(2), β = 96.44(2), γ = 69.45(2)°, V = 3045(1) Å³, Z = 2, D_c = 1.185 g cm⁻³, R = 0.067, R_w = 0.063 for 5269 reflections [$I > 3\sigma(I)$, 2θ_{max} = 55.0°, 2θ–ω scan, 23 °C].

5: C₆₀H₈₄N₃S₃Yb, M_r = 1116.59, monoclinic, space group $P2_1/n$ with a = 20.402(3), b = 16.654(3), c = 22.258(3) Å, β = 117.10(1)°, V = 6731(1) Å³, Z = 4, D_c = 1.102 g cm⁻³, R = 0.081, R_w = 0.106 for 4928 reflections [$I > 3\sigma(I)$, 2θ_{max} = 55.0°, 2θ–ω scan, 23 °C].

Atomic coordinates, bond lengths and angles, and thermal parameters for **1**, **2**, **4b** and **5** have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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