

Monocyclooctatetraenyl(thiolato)samarium(III) Complexes from the Reaction of Metallic Samarium with Cyclooctatetraene and Diaryldisulfide: Crystal Structures of $[\text{Sm}(\mu\text{-SPh})(\text{C}_8\text{H}_8)(\text{thf})_2]_2$ and $[\{\text{Sm}[\mu\text{-S}(2,4,6\text{-triisopropylphenyl})](\text{C}_8\text{H}_8)(\text{thf})\}_2]$

Kazushi Mashima,^a Yuushou Nakayama,^a Nobuko Kanehisa,^b Yasushi Kai^b and Akira Nakamura^{*a}

^a Department of Macromolecular Science, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan

^b Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan

Metallic samarium reacts directly with cyclooctatetraene in the presence of diaryldisulfide to give cyclooctatetraenyl(thiolato)samarium(III) complexes, $[\text{Sm}(\mu\text{-SAr})(\text{C}_8\text{H}_8)(\text{thf})_n]_2$ (thf = tetrahydrofuran) (**1**, Ar = C₆H₅, $n = 2$; **2**, Ar = 2,4,6-Me₃-C₆H₂, $n = 2$; **3**, Ar = 2,4,6-(Prⁱ)₃-C₆H₂, $n = 1$), the structures of which are confirmed by single crystal X-ray analyses of **1** and **3**, while Yb reacts with diphenyldisulfide in thf to afford $[\text{Yb}(\text{SPh})_2(\text{thf})]_n$.

Mono- and bis(cyclooctatetraenyl)lanthanide(III) halides have been prepared mainly by the reaction of lanthanide halides with cyclooctatetraene dianion. The ligand exchange reaction of such cyclooctatetraenyl lanthanide complexes with various anions is reported to give a series of complexes of the type, $(\text{C}_8\text{H}_8)\text{Ln}(\text{X})$.¹⁻⁷ We have reported previously that the reaction of lanthanide metals with C₈H₈ in the presence of iodine afforded $\text{LnI}(\eta\text{-C}_8\text{H}_8)(\text{thf})_n$.⁸ In this communication, we report a simple and convenient synthetic route to trivalent lanthanide thiolate complexes bearing a cyclooctatetraenyl ligand. The structures of benzenethiolate and 2,4,6-triisopropylbenzenethiolate complexes of samarium are revealed, which are the first structurally characterized lanthanide(III) thiolate complexes having a cyclooctatetraenyl ligand.⁹⁻¹³

Treatment of metallic samarium with 1 equiv. of cyclooctatetraene and 1 equiv. of diphenyldisulfide in thf at 50 °C for 24 h in the presence of a catalytic amount of iodine afforded the deep blue-purple solution of $[\text{Sm}(\mu\text{-SPh})(\eta\text{-C}_8\text{H}_8)(\text{thf})_2]_2$ **1**.[†] The complex **1** was obtained as deep-purple prisms in 76% yield upon crystallization from the saturated thf solution. Similarly, monocyclooctatetraenyl(thiolato)samarium complexes, $[\text{Sm}(\mu\text{-SC}_6\text{H}_2\text{Me}_3\text{-2,4,6})(\eta\text{-C}_8\text{H}_8)(\text{thf})_2]_2$ **2**[†] and $[\text{Sm}(\mu\text{-SC}_6\text{H}_2\text{Pr}^i\text{-2,4,6})(\eta\text{-C}_8\text{H}_8)(\text{thf})_2]_2$ **3**[†] were prepared in 34 and 25% yield, respectively Scheme 1. In the course of these reactions, a polymeric Sm^{II} complex, $[\text{Sm}(\eta\text{-C}_8\text{H}_8)(\text{thf})]_n$ **4**,⁸ was precipitated, and then gradually disappeared. Thus, the reaction of **4** with diphenyldisulfide resulted in the formation of **1** in modest yield. Some

organosamarium(II) complexes bearing cyclopentadienyl derivatives have been reported to react with iodine, dialkyldisulfide, and other oxidants.^{10,14-17}

In the case of ytterbium, we obtained a red, insoluble powder in 91% yield by the reaction of Yb and diphenyldisulfide with and without cyclooctatetraene. This compound was formulated as $[\text{Yb}(\text{SPh})_2(\text{thf})]_n$ **5**[†] since the hydrolysis of the product gave benzenethiol and thf in 2 : 1 molar ratio. Further characterization by solution NMR of this complex was hampered by its insolubility in thf. Similarly, the benzene-selenolate complex of monocyclooctatetraenylsamarium, $[\text{Sm}(\mu\text{-SePh})(\eta\text{-C}_8\text{H}_8)(\text{thf})_2]_2$ **6**,[†] was also prepared in 46%

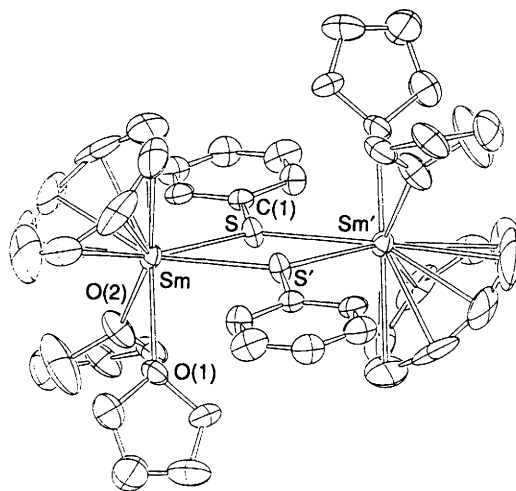
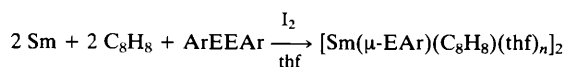


Fig. 1 Complex **1**. Thermal ellipsoids scaled at 30% probability level. Selected bond distances (Å) and angles (degree): Sm-S = 2.914(8), Sm-S' = 2.934(8), Sm-O(1) = 2.55(1), Sm-O(2) = 2.58(2), Sm-C(C₈H₈) = av. 2.67(4); S-Sm-S' = 63.6(1), Sm-S-Sm' = 116.4(1), Sm-S-C(1) = 122.8(7), Sm'-S-C(1) = 119.9(7), S-Sm-O(1) = 108.0(4), S'-Sm-O(1) = 77.3(4), S-Sm-O(2) = 79.1(4), S'-Sm-O(2) = 118.0(5).



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|---|---------|
| 1: EAr = SC ₆ H ₅ , | $n = 2$ |
| 2: EAr = SC ₆ H ₂ Me ₃ -2,4,6, | $n = 2$ |
| 3: EAr = SC ₆ H ₂ Pr ⁱ -2,4,6, | $n = 1$ |
| 6: EAr = SeC ₆ H ₅ | $n = 2$ |

Scheme 1

[†] Synthesis of $[\text{Sm}(\text{SPh})(\text{C}_8\text{H}_8)(\text{THF})_2]_2$ **1**: To a mixture of samarium metal powder (0.36 g, 2.43 mmol), cyclooctatetraene (0.30 ml, 2.66 mmol) and diphenyl disulfide (0.28 g, 1.27 mmol) in thf (40 ml) was added a catalytic amount of iodine (19 mg, 0.07 mmol) to activate metal surface. The reaction mixture was stirred at 50 °C. A clear, deep-violet solution resulted in 24 h. Filtration of the mixture and cooling of the filtrate to -20 °C for 1 day afforded deep-purple prisms of **1** in 76% (0.94 g) yield.

These complexes were characterized by ¹H NMR, but difficult to be characterized by elemental analysis. The chemical shifts depend on temperature and concentration. ¹H NMR (270 MHz, [²H₈], 30 °C, 5 mg ml⁻¹) spectroscopic data: **1**: δ 11.24 (s, 16H, C₈H₈), 10.41 (s, 4H, o-H), 7.99 (s, 4H, m-H), 7.83 (s, 2H, p-H). **2**: δ 11.19 (s, 16H, C₈H₈), 8.07 (s, 4H, m-H), 4.66 (s, 12H, o-Me), 2.65 (s, 6H, p-Me). **3**: δ 11.27 (s, 16H, C₈H₈), 7.95 (s, 4H, m-H), 7.08 (m, 4H, o-CHMe₂), 3.33 (m, 2H, p-CHMe₂), 2.25 (d, 24H, o-CHMe₂), 1.21 (d, 12H, p-CHMe₂). **6**: δ 11.49 (s, 16H, C₈H₈), 9.74 (s, 4H, o-H), 7.71 (s, 6H, m- and p-H).

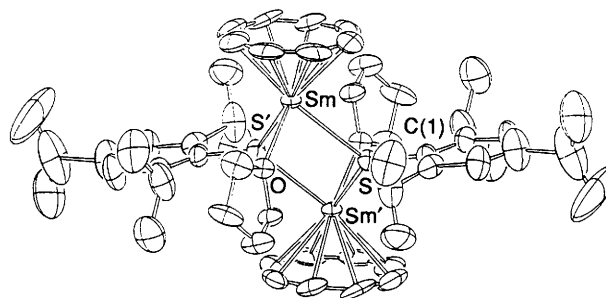


Fig. 2 Complex **3**. Thermal ellipsoids scaled at 30% probability level. Selected bond distances (Å) and angles (degree): Sm-S = 2.891(6), Sm-S' = 2.874(5), Sm-O = 2.53(1), Sm-C(C₈H₈) = av. 2.64(3); S-Sm-S' = 74.7(2), Sm-S-Sm' = 105.3(2), Sm-S-C(1) = 121.0(8), Sm'-S-C(1) = 133.0(8), S-Sm-O = 87.1(4), S'-Sm-O = 88.4(3).

yield. Although these thiolate and selenolate complexes decomposed rapidly upon exposure to oxygen or moisture, they were thermally quite stable in solution.

The molecular structures of compound **1** and **3** are shown in Fig. 1 and 2, respectively;‡ Both compounds have thiolate-bridged binuclear structure in which each monomer moiety is related by the centrosymmetry. The Sm₂S₂ unit is planar, and the sulfur atoms of thiolates are surrounded by two samarium atoms and a carbon atom of the phenyl group, and these four atoms are in a plane because the summation of angles around sulfur atom is 359.1° for **1** and 359.3° for **3**, respectively. The samarium atom has a pseudo-square pyramidal geometry in **1**, while it has pseudo-tetrahedral geometry in **3**. Thus, the geometry of samarium atom depends on the steric effect of the thiolate ligand.

The C₈H₈ coordinates to samarium in η⁸-fashion and is planar. The bond distances between Sm and carbons of C₈H₈ [2.63(2) to 2.72(4) Å for **1** and from 2.61(3) to 2.70(3) Å for **3**] are normal.¹⁸ The bond distances [2.892(6) and 2.874(5) Å] of Sm–S of **3** are somewhat shorter than those [2.899(8) and 2.949(8) Å] of **1**. These Sm–S bond distances of dimeric complexes **1** and **3** are longer than those of monomeric samarium complexes, Sm(SC₆H₂Bu^t₃-2,4,6)₃ [2.646(7), 2.652(9) and 2.634(9) Å]¹² and [Li(tmeda)]₃[Sm(S-Bu^t)₆

[2.838(3), 2.821(3), and 2.821(3) Å, tmeda = *N,N,N',N'*-tetramethylethylenediamine].¹³ The S–Sm–S' bond angle of **3** [75.6(3)°] is larger than that of **1** [63.6(1)°], depending on the geometry.

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References

- 1 F. Mares, K. O. Hodgson and A. Streitwieser, Jr., *J. Organomet. Chem.*, 1970, **24**, C68; K. O. Hodgson, F. Mares, D. F. Starks and A. Streitwieser, Jr., *J. Am. Chem. Soc.*, 1973, **95**, 8650; K. O. Hodgson and K. N. Raymond, *Inorg. Chem.*, 1972, **11**, 171.
- 2 J. D. Jamerson, A. P. Masino and J. Takats, *J. Organomet. Chem.*, 1974, **65**, C33.
- 3 W. Ke, J. Zhongsheng and C. Wenqi, *J. Chem. Soc., Chem. Commun.*, 1991, 680.
- 4 P. Bruin, M. Booi, J. H. Teuben and A. Oskam, *J. Organomet. Chem.*, 1988, **350**, 17; M. Booi, N. H. Kiers, H. J. Heeres and J. H. Teuben, *J. Organomet. Chem.*, 1989, **364**, 79.
- 5 H. Schumann, R. D. Köhn, F.-W. Reier, A. Dietrich and J. Pickardt, *Organometallics*, 1989, **8**, 1388; H. Schumann, C. Janiak, R. D. Köhn, J. Loebel and A. Dietrich, *J. Organomet. Chem.*, 1989, **365**, 137.
- 6 A. L. Wayda, *Organometallics*, 1983, **2**, 565; A. L. Wayda and R. D. Rogers, *Organometallics*, 1985, **4**, 1440.
- 7 U. Kilimann and F. T. Edlmann, *J. Organomet. Chem.*, 1993, **444**, C15.
- 8 K. Mashima and H. Takaya, *Tetrahedron Lett.*, 1989, **30**, 3697.
- 9 H. C. Aspinall, D. C. Bradley, M. B. Hursthouse, K. D. Sales and N. P. C. Walker, *J. Chem. Soc., Chem. Commun.*, 1985, 1585.
- 10 A. Zalkin, T. J. Henly and R. A. Anderson, *Acta Crystallogr., Sect. C*, 1987, **43**, 233; D. J. Berg, R. A. Anderson and A. Zalkin, *Organometallics*, 1988, **7**, 1858; S. D. Stults, R. A. Anderson, and A. Zalkin, *Organometallics*, 1990, **9**, 1623.
- 11 H. Schumann, I. Albrecht, M. Gallagher, E. Hahn, C. Munchmore and J. Pickardt, *J. Organomet. Chem.*, 1988, **349**, 103.
- 12 B. Cetinkaya, P. B. Hitchcock, M. F. Lappert and R. G. Smith, *J. Chem. Soc., Chem. Commun.*, 1992, 932.
- 13 K. Tatsumi, T. Amemiya, H. Kawaguchi and K. Tani, *J. Chem. Soc., Chem. Commun.*, 1993, 773.
- 14 S. P. Nolan, D. Stern and T. J. Marks, *J. Am. Chem. Soc.*, 1989, **111**, 7844.
- 15 S. A. Kinsley, A. Streitwieser and A. Zalkin, *Organometallics*, 1985, **4**, 52.
- 16 R. G. Hayes and J. L. Thomas, *J. Am. Chem. Soc.*, 1969, **91**, 6876.
- 17 F. T. Edlmann, M. Rieckhoff, I. Haiduc and I. Silaghi-Dumitrescu, *J. Organomet. Chem.*, 1993, **447**, 203.
- 18 H. Schumann, J. Winterfeld, F. Görlitz and J. Pickardt, *J. Chem. Soc., Chem. Commun.*, 1993, 623.

‡ Crystal data for **1**: C₄₄H₅₈O₄S₂Sm₂, M_w = 1015.79, crystal size 0.30 × 0.25 × 0.25, orthorhombic, space group *Pbca* with *a* = 18.762(5), *b* = 15.383(5), *c* = 14.775(4) Å, V = 4264(4) Å³, Z = 4, D_c = 1.582 g cm⁻³, 5435 reflections (2θ_{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 direct method and refined by full-matrix least-squares analysis (TEXSAN package of Molecular Structure Corporation) to R = 0.050, R_w = 0.071. H-atoms were located at the calculated positions and not refined.

For **3**: C₅₄H₇₈O₂S₂Sm₂, M_w = 1124.06, crystal size 0.60 × 0.40 × 0.10, monoclinic, space group *C2/c* with *a* = 26.820(3), *b* = 10.793(3), *c* = 21.122(2) Å, β = 98.424(8)°, V = 6048(2) Å³, Z = 4, D_c = 1.234 g cm⁻³, 7474 reflections (2θ_{max} = 55.0°, 2θ–ω scan, 23 °C) collected on a Rigaku AFC-5R diffractometer using Mo-Kα radiation, empirical absorption correction carried out based on an azimuthal scan. Structure solved by the direct method and refined by full-matrix least-squares analysis (TEXSAN package) to R = 0.073, R_w = 0.098. H-atoms were located at the calculated positions and not refined.

Atomic coordinates, bond lengths and angles, and thermal parameters of **1** and **3** have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.