Synthesis and Structures of Homoleptic 2-Methylpropane-2-thiolate Complexes of Samarium and Ytterbium

Kazuyuki Tatsumi,* Takao Amemiya, Hiroyuki Kawaguchi and Kazuhide Tani

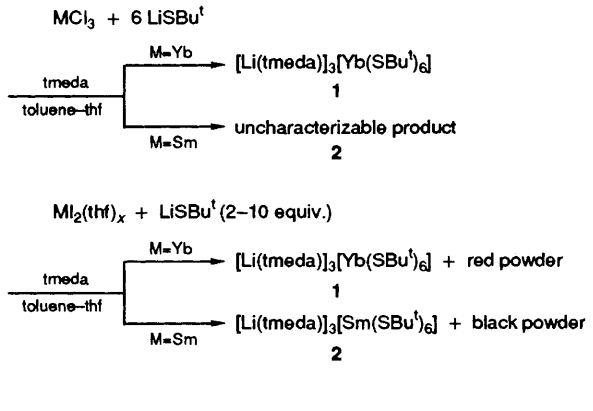
Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560, Japan

The homoleptic 2-methylpropane-2-thiolate complexes $[Li(tmeda)]_3[Ln(SBu^t)_6]$ (Ln = Yb **1** and Sm **2** have been synthesized and structurally characterized; **1** from the reaction of $YbCl_3$ or $YbI_2(thf)_x$ with $LiSBu^t$, and **2** from $SmI_2(thf)_x$ and $LiSBu^t$, in the presence of *N,N,N′,N′*-tetramethylethylenediamine (tmeda; thf = tetrahydrofuran).

Syntheses of lanthanide thiolates are still scarce,[1–5] and the bonds between 'soft' sulfur donors and 'hard' 4f elements have been thought unstable. This is perhaps more often presumed than actually proved. There is a good number of thermally stable homoleptic thiolate and dithiolate complexes of d^0 group 4 and 5 metals,[6–10] despite the hardness of such d^0 early metals, and one may anticipate that the related 'd^0' lanthanides could form stable M–S bonds as well. Very recently, the first homoleptic thiolate complex of a lanthanide, $[Sm(SC_6H_2Bu^t_3\text{-}2,4,6)_3]$, and the related intriguing Yb^{II} thiolate, $[Yb(SC_6H_2Bu^t_3\text{-}2,4,6)_2(dme)_2]$ (dme = dimethoxyethane), were reported.[11] Also a 'd^0' 5f element, uranium(IV), was found to form a thermally stable homoleptic ethanedithiolate complex, $[Li(dme)]_4[U(SCH_2CH_2S)_4]$.[12] We now report the synthesis and X-ray structures of homoleptic 2-methylpropane-2-thiolate complexes of samarium and ytterbium, $[Li(tmeda)]_3[Ln(SBu^t)_6]$ (Ln = Yb **1** and Sm **2**; tmeda = *N,N,N′,N′*-tetramethylethylenediamine).

Treatment of $YbCl_3$ with 6–10 equiv. of $LiSBu^t$ in toluene–tetrahydrofuran (thf) in the presence of *ca.* 5 equiv. of tmeda generated a clear yellow–orange solution. Evaporation of the solvent, extraction of the solid residue with toluene, and recrystallization from the same solvent yielded **1** as yellow crystals in 90% yield. This is the simplest route to homoleptic lanthanide thiolates, and addition of tmeda seems to be important for isolation of the thiolate complex in a crystalline form. In the absence of tmeda, the reaction yielded a yellow–orange solid which appears to contain an analogous ytterbium thiolate complex according to the ^1H NMR and IR spectra, but its purification has been unsuccessful. Attempts to synthesize an analogous samarium thiolate from the $SmCl_3$–$LiSBu^t$–tmeda reaction system did not give a characterizable product.

We then examined reactions of the divalent lanthanides, $YbI_2(thf)_x$ and $SmI_2(thf)_x$, with $LiSBu^t$. Addition of a thf solution of $LiSBu^t$ (6–10 equiv.) to a toluene–thf suspension of $YbI_2(thf)_x$ with *ca.* 5 equiv. of tmeda immediately gave a homogeneous red solution. Upon stirring the solution for a few hours, the red colour turned gradually to orange and an air-sensitive fine, red powder precipitated. From the solution phase, **1** was obtained in 60–70% yield. Similarly the SmI_2–$LiSBu^t$–tmeda reaction system in toluene–thf gave rise at first to a clear, black solution, and then a gradual colour change to yellow ensued with a formation of a black precipitate. The samarium thiolate complex **2** was isolated as yellow crystals in 70% yield. Even if the amount of $LiSBu^t$ was reduced to 2 equiv. per Yb or Sm, the isolated product was **1** or **2**.



Evidently, the lanthanides are oxidized during the reactions, and we think C–S bond cleavage and concomitant electron transfer and/or disproportionation reactions promote the oxidation. The red (Yb) and black (Sm) precipitates were found to contain lithium, sulfide, 2-methylpropane-2-thiolate and iodide, but not tmeda. Unfortunately, further characterization was hampered by their low solubility in organic solvents. Formation of the trivalent lanthanide thiolate complexes from $YbI_2(thf)_x$ and $SmI_2(thf)_x$ contrasts to retention of the divalent oxidation state of Yb in the reaction of $[Yb\{N(SiMe_3)_2\}(dme)_2]$ with $HSC_6H_2Bu^t_3$-2,4,6 to give $[Yb(SC_6H_2Bu^t_3\text{-}2,4,6)_2(dme)_2]$.

The molecular structure of **1** is shown in Fig. 1. Compound **2** is isomorphous and nearly isometric to **1**, and only selected bond distances and angles of **2** are given as well at those of **1** in the figure caption.† The M = Yb/Sm atom resides in the centre of the molecule, to which six SBu^t ligands are bound. Three lithium cations surround this $[M(SBu^t)_6]^{3-}$ anion, in such a way that each bridges two thiolate sulfurs and the MS_6Li_3 skeleton assumes a three-bladed propeller configuration. A tmeda ligand further coordinates to each lithium and completes the tetrahedral coordination geometry at Li. The crystallographic twofold axis passes through M and Li(2). Thus, two trigonal faces defined by S(1), S(2), S(3′) and S(1)′, S(2′), S(3) are precisely parallel, and so are the MLi_3 plane and these S_3 triangles. The averaged trigonal-twist (S–C_t–C_t′–S) angle of 36.5° (for **1** and **2**), where C_t and C_t′ are the triangle centres, is very close to the corrected octahedral twist (36.0°) based on the bidentate bite of b = 1.16 (**1**), 1.12 (**2**).[13] The mean Yb–S bond length of 2.737(2) Å is close to that of $[Yb(SC_6H_2Bu^t_3\text{-}2,4,6)_2(dme)_2]$ [2.756(8) Å],[11] and is longer

† *Crystal structure analysis* of **1**: single crystal 0.25 × 0.3 × 0.4 mm³, monoclinic space group *C2/c*, a = 19.328(8), b = 14.427(2), c = 27.424(4) Å, β = 101.26(3)°, V = 7500(3) Å³, Z = 4, D_c = 1.12 Mg m⁻³. Data collection with a Rigaku AFC5R diffractometer; Mo-Kα radiation, ω scan, 2θ = 4–60°, 9562 measured reflections, 9246 independent, 6067 observed ($I > 3.0\ \sigma I$), empirical absorption correction based on azimuthal scans. Solution and refinement with the TEXSAN package of Molecular Structure Corporation (direct methods); all non-hydrogen atoms except for the toluene solvate were refined anisotropically and hydrogen atoms of SBu^t and tmeda were put at calculated positions; the methyl group of toluene was not located due to disorder; full matrix, refined parameters 287, R = 0.052 and R_w = 0.064, goodness of fit = 2.04.

Crystal structure analysis of **2**: single crystal 0.2 × 0.3 × 0.4 mm³, monoclinic space group *C2/c*, a = 19.36(2), b = 14.472(4), c = 27.607(9) Å, β = 101.70(7)°, V = 7575(7) Å³, Z = 4, D_c = 1.09 Mg m⁻³. Data collection with a Rigaku AFC5R diffractometer; Mo-Kα radiation, ω scan, 2θ = 4–50°, 7249 independent, 4318 observed ($I > 3.0\sigma I$), empirical absorption correction based on azimuthal scans. Solution and refinement with SHELX76 and SHELX86 programs (direct methods); all non-hydrogen atoms were refined anisotropically and hydrogen atoms, except for toluene, were put at calculated positions; the methyl group of toluene was not located; full matrix, refined parameters, 318, R = 0.084 and R_w = 0.087.

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

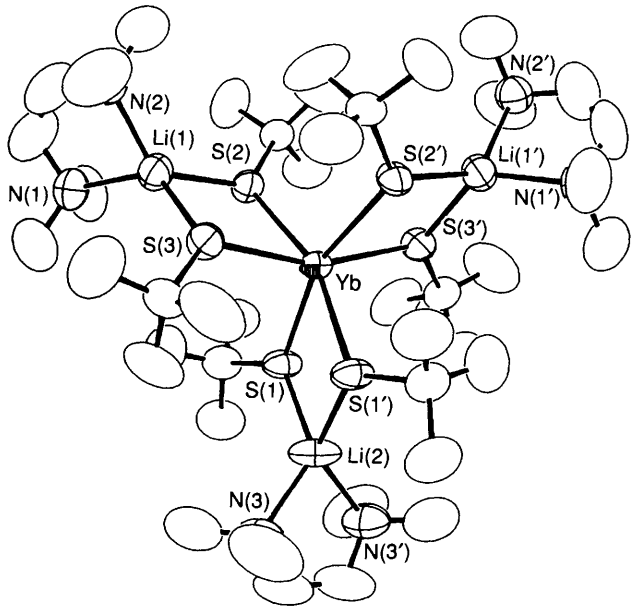


Fig. 1 The molecular structure of $[Li(tmeda)]_3[Yb(SBu^t)_6]$ **1** showing 50% thermal ellipsoids. The structure of $[Li(tmeda)]_3[Sm(SBu^t)_6]$ **2** is isomorphous. Selected bond distances (Yb/Sm, Å) and angles (Yb/Sm, °): M–S(1) 2.744(2)/2.838(3), M–S(2) 2.730(2)/2.821(3), M–S(3) 2.737(2)/2.821(3), S(1)–Li(2) 2.39(1)/2.34(2), S(2)–Li(1) 2.38(1)/2.39(2), S(3)–Li(1) 2.38(1)/2.37(2), Li(1)–N(1) 2.18(1)/2.18(2), Li(1)–N(2) 2.15(1)/2.16(2), Li(2)–N(3) 2.15(1)/2.22(2); S(1)–M–S(1') 70.83(7)/70.3(1), S(2)–M–S(3) 70.98(5)/70.1(1), S(1)–Li(2)–S(1') 81.2(4)/88.7(9), S(2)–Li(1)–S(3) 83.4(5)/86.0(7), N(1)–Li(1)–N(2) 84.6(5)/83.8(8), N(3)–Li(2)–N(3') 83.3(7)/82(1).

than the two mean Yb–S distances of $[Yb(C_5Me_5)_2(SC_6H_5)(NH_3)]$ [2.670(3) Å and 2.679(3) Å; two molecules in an asymmetric unit].[3] For the two isostructural molecules, **1** and **2**, the Yb complex has M–S bonds 0.090(3) Å shorter than the Sm analogue. The difference accords well with the difference (0.09 Å) of the ionic sizes of Yb and Sm.[14] Within each S–Li–S 'chelate', the averaged S···S non-bonding distance is 3.175 Å for both **1** and **2**, so that the mean S–M–S bite angle is slightly smaller (by 0.7°) for **2**.

Although the two compounds **1** and **2** are air/moisture sensitive, they do not show any sign of decomposition in toluene at 100 °C. The 270 MHz ^1H NMR spectra in C_6D_6 are featured by three relatively broad resonances arising from tmeda [methyl, δ 2.16 (sh) **1**, 2.16 ($\nu_{1/2}$ 4.4 Hz) **2**; ethylene, δ 1.64 ($\nu_{1/2}$ 8.9 Hz) **1**, 1.48 ($\nu_{1/2}$ 9.8 Hz) **2**] and SBu^t protons [δ 2.22 **1**, 2.27 ($\nu_{1/2}$ 12.4 Hz) **2**]. The significant up-field shift of the ethylene proton signals of tmeda upon coordination to lithium, which results in reversal of the methyl and ethylene resonances, has been observed in the lithiated chalcogenide complexes, $[Li_2(tmeda)_2S_6]$, $[Ta(\eta^5\text{-}C_5Me_5)S_3Li_2(tmeda)_2]$ and $[Ta(\eta^5\text{-}C_5Me_5)Se_3Li_2(tmeda)_2]$.[15] And the solid state structures of **1** and **2** are probably retained in solution.

Received, 12th January 1993; Com. 3/00209H

References

1 H. C. Aspinall, D. C. Bradley, M. B. Hursthouse, K. D. Sales and N. P. C. Walker, *J. Chem. Soc., Chem. Commun.*, 1985, 1585.
2 H. Schumann, I. Albrecht and E. Hahn, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 985; H. Schumann, I. Albrecht, M. Gallagher, E. Hahn, C. Munchmore and J. Pickardt, *J. Organomet. Chem.*, 1988, **349**, 103.
3 A. Zalkin, T. J. Henly and R. A. Andersen, *Acta Crystallogr., Sect. C*, 1987, **43**, 233.
4 S. D. Stult, R. A. Andersen and A. Zalkin, *Organometallics*, 1990, **9**, 1623.
5 R. S. Saxena and S. S. Sheelwant, *J. Inorg. Nucl. Chem.*, 1973, **35**, 3963; R. S. Saxena and V. K. Bhatia, *J. Inorg. Nucl. Chem.*, 1975, **37**, 309; S. Kapur, B. L. Kalsotra and R. K. Multani, *J. Inorg. Nucl. Chem.*, 1973, **35**, 3966.
6 M. Bochmann, I. Hawkins and L. M. Wilson, *J. Chem. Soc., Chem. Commun.*, 1988, 344.
7 J. R. Dorfman, Ch. P. Rao and R. H. Holm, *Inorg. Chem.*, 1985, **24**, 454.
8 J. L. Martin and J. Takats, *Inorg. Chem.*, 1975, **14**, 73; M. Cowie and M. J. Bennett, *Inorg. Chem.*, 1975, **14**, 1589.
9 K. Tatsumi, Y. Sekiguchi, A. Nakamura, R. E. Cramer and J. J. Rupp, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 86; K. Tatsumi, I. Matsubara, Y. Sekiguchi, A. Nakamura and C. Mealli, *Inorg. Chem.*, 1989, **28**, 773; K. Tatsumi, I. Matsubara, Y. Inoue, A. Nakamura, K. Miki and N. Kasai, *J. Am. Chem. Soc.*, 1989, **111**, 7766.
10 S.-M. Koo, R. Bergero, A. Salifoglou and D. Coucouvanis, *Inorg. Chem.*, 1990, **24**, 4844.
11 B. Çetinkaya, P. B. Hitchcock, M. F. Lappert and R. G. Smith, *J. Chem. Soc., Chem. Commun.*, 1992, 932.
12 K. Tatsumi, I. Matsubara, Y. Inoue, A. Nakamura, R. E. Cramer, G. J. Taogoshi, J. A. Golen and J. W. Gilje, *Inorg. Chem.*, 1990, **29**, 4928.
13 D. L. Kepert, *Inorg. Chem.*, 1972, **11**, 1561.
14 R. D. Shannon, *Acta Crystallogr., Sect. A*, 1976, **32**, 751.
15 K. Tatsumi, Y. Inoue, A. Nakamura, R. E. Cramer, W. Van-Doorne and J. W. Gilje, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 422; A. J. Banister, D. Barr, A. T. Brooker, W. Clegg, M. C. Cunnington, M. J. Doyle, S. R. Drake, W. R. Gill, K. Manning, P. R. Raithby, R. Snaith, K. Wade and D. S. Wright, *J. Chem. Soc., Chem. Commun.*, 1990, 105; K. Tatsumi, Y. Inoue, H. Kawaguchi, M. Kohsaka, A. Nakamura, R. E. Cramer, W. Van-Doorne, G. J. Taogoshi and P. N. Richmann, *Organometallics*, 1993, **12**, 352; K. Tatsumi, H. Kawaguchi, K. Tani, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, in the press.