The First Isolation and Structural Analysis of Chalcogenocarboxylato Samarium Complexes, [(RCOS)$_3$Sm(thf)$_2$] and [Na(thf)$_4$] [Sm(RCSS)$_4$]; The Alkali Metal Salt-Like Reaction and the Insertion Reaction of Imine to the Sm-S Bond

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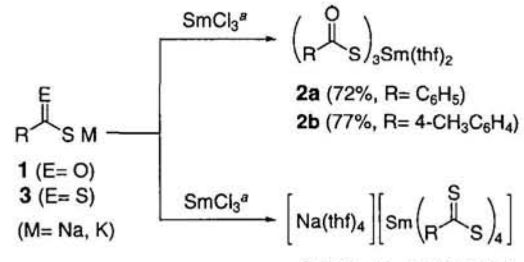
The first chalcogenocarboxylato lanthanid complexes, [(RCOS)$_3$Sm(thf)$_2$] and [Na(thf)$_4$][Sm(RCSS)$_4$](R= 4-MeC$_6$H$_4$) were isolated and characterized crystallographically. They exhibit an alkali metal salt-like reaction such as *S*-esterification and an insertion reaction of C=N to the Sm-S bond.

A large number of carboxylato lanthanid complexes have been prepared and their structures have been revealed.[1] During the last two decades, the chemistry of typical element and transition-metal chalcogenocarboxylates has been extensively investigated,[2] in part because of their possible relevance to the structure, bonding and function of biologically active centers in metalloprotein such as ferrodoxines and nitrogenase etc. In contrast, there has been little known about the lanthanid complexes, most likely due to the difficulty of their preparation and purification. We now report the first isolation and X-ray structural analysis of thio- **2** and dithiocarboxylato samarium complexes **4** and their characteristic *S*-esterification reaction, similar to that of the corresponding alkali metal salts.

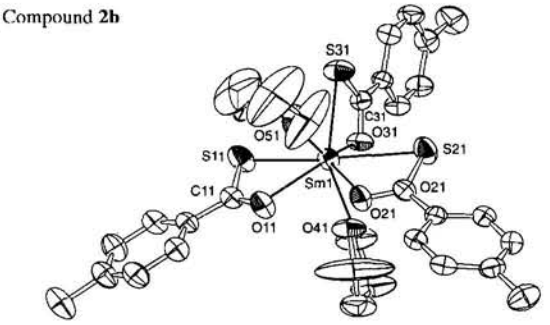
Scheme 1.



^{a}Conditions: **1** / SmCl$_3$ = 3 : 1 and **3** / SmCl$_3$ = 4 : 1 in THF, reflux, 5 h.

Tris(4-methylbenzenecarbothioato)samarium(III) **2b** was synthesized in 77% yield as pale yellow crystals by the reaction of the corresponding potassium thiocarboxylate **1b** with 1.05 equiv of SmCl$_3$. The similar reaction with sodium 4-methylbenzenecarbodithioate **3** (M= Na) under the same conditions led to a 75% yield of sodium tetrakis(4-methylbenzenecarbodithioato)samarium(III) **4** as deep-red crystals. These complexes are the first chalcogenocarboxylato lanthanid complexes. Attempts to prepare tris(dithiocarboxylato)samarium [(RCSS)$_3$Sm(III)(thf)$_2$] **5** and sodium tetrakis(thiocarboxyl-ato)samarium(III) [Na(thf)$_4$][Sm(RCOS)$_4$] **6** have been unsuccessful under various conditions. Complexes **2** and **4** were characterized by IR, and ^{1}H and ^{13}C NMR spectra and finally determined by X-ray diffraction analysis (Figure 1, **a** and **b**).[4]

(a) Compound **2b**



(b) Compound **4**

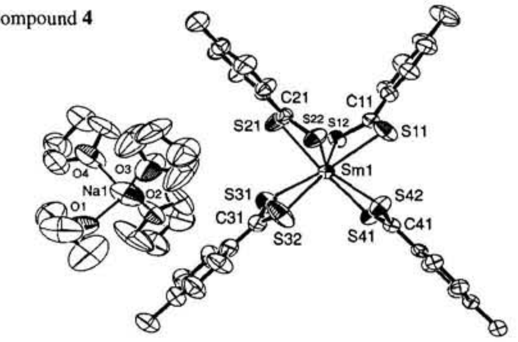
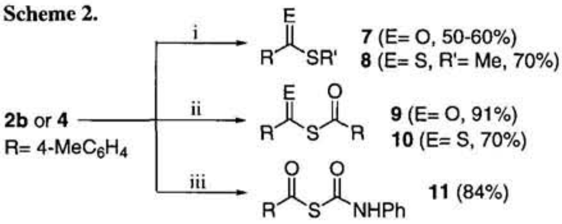


Figure 1. ORTEP drawings of **2b** (**a**) and **4** (**b**). Atoms are shown as 50% probability thermal ellipsoid. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [deg]: **2b**: Sm1–S11 2.877(2), Sm1–O11 2.408(3), Sm1–O41 2.444(3), S11–C11 1.705(5), O11–C11 1.254(6), S11–Sm1–O11 57.52(9), O11–C11–S11 120.3(4). **4**: Sm1–S11 2.816(2), Sm1–S22 2.930(2), S11–C11 1.694(7), S12–C11 1.681(7), S22–C21 1.679(7), S21–C21 1.686(7), O1–Na1 2.258(7), O2–Na1 2.344(9), Sm1···Na1 7.48, S11–C11–S12 121.0(4), S11–Sm1–S12 61.35(6), Sm1–S12–C11 86.5(3).

2b is 8 coodination and a distorted dodecahedral geometry where with the three thiocarboxylate groups and two THF molecules coordinate. The distance (average 2.43 Å) between the carbonyl oxygen and Sm are significantly shorter than those reported elsewhere.[5] The C=O length (1.25-1.26 Å) is significantly longer than those of [PhC(O)SLi • TMEDA]$_2$ (1.246 Å)[6a] and MeC(O)SK (1.23 Å),[6b] which are highly ionic. **4** consists of sodium cation with four THF molecules and samarium with the four dithiocarboxyl groups.[7] The samarium is 8 coordination and a dodecahedral geometry where the two dithiocarboxylato ligands are located in the same plane. The difference in the Sm–S distances is average 0.12 Å for the former dithiocarboxylate pair, while that of the other pair is average 0.06 Å. The one dithiocarboxylate ligand has a different C–S distance,1.656 and 1.720 Å, indicating the double and single bonds, respectively. The C–S distances of three the other dithiocarboxylate ligands are nearly the same.

Thio-, dithio- and seleno-carboxylato complexes of transition-metal hardly react with alkyl halides.[8] In contrast, **2** and **4** were found to readily react with alkyl and allyl iodides at room temperature to give thioesters **7** and dithioesters **8** in good yields, respectively.[9] (Scheme 2) The reaction with 4-methylbenzoyl chloride more smoothly proceeds to give the moderate to good yields of synmetrical di(acyl) **9** and unsymmetrical acyl thioacyl sulfides **10**.[9] These results clearly indicate that **2** and **4** exhibit the same reaction mode with the corresponding alkali metal salts [RC(O)E M: E= S, Se, Te; M= alkali metal] which are highly ionic.[10] Furthermore, the reaction of **2b** with PhNCO, followed by an aqueous workup, led to a 84% yield of *N*-phenylcarbamoyl 4-methylbenzoyl sulfide **11**,[9] which is considered to be formed by the insertion reaction of the isocyanate into the Sm–S bond, although the insertion of alkenes into the lanthanid–carbon bond has been documented.[11]

Scheme 2.



Conditions: i, MeI 5 mL, 20 °C, 2 h; ii, 4-$\mathrm{MeC_6H_4C(O)Cl}$ (1 equiv), THF, 20 °C, 1 h; iii, PhNCO (1 equiv) in THF, reflux, 22 h.

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3 **2a**: mp 105-117 °C (dec.); IR (KBr) 1464 (νC=O) cm^{-1}; ^{1}H NMR [$\mathrm{(CD_3)_2CO}$] δ 1.75-1.80 (m, 8H, THF), 3.59-3.63 (m, 8H, THF), 7.62-7.65 (br, 9H, Ar), 8.84 (br, 6H, Ar); ^{13}C NMR [$\mathrm{(CD_3)_2CO}$] δ 26.3, 68.2 (THF), 128.3, 128.6, 133.0, 142.0 (Ar), 227.6 (C=O). Anal. Found: C, 49.33; H, 4.43%. Calcd for $\mathrm{C_{29}H_{31}O_5S_3Sm}$: C, 49.56; H, 4.30%. **2b**: 2THF: mp 157-169 °C (dec.); IR (KBr) 1458 (νC=O) cm^{-1}; ^{1}H NMR [$\mathrm{(CD_3)_2CO}$] δ 1.74-1.77 (m, 8H, THF), 2.49 (s, 9H, $\mathrm{CH_3}$), 3.56-3.59 (br, 8H, THF), 7.46 (br, 6H, Ar), 8.81 (br, 6H, Ar); ^{13}C NMR [$\mathrm{(CD_3)_2CO}$] δ 21.9 ($\mathrm{CH_3}$), 26.4, 68.4 (THF), 128.8, 129.7, 140.2, 144.4 (Ar), 228.2 (C=O); UV/vis $\lambda_{\max}$ (log ε) (THF) 214 (5.89), 248 (5.84), 343 (5.30) nm. Anal. Found: C, 51.09; H, 4.84%. Calcd for $\mathrm{C_{32}H_{37}O_5S_3Sm}$: C, 51.37; H, 4.98%. **4**: mp 208-212 °C (dec.); IR (KBr) 1016 (νC=S) cm^{-1}; ^{1}H NMR [$\mathrm{(CD_3)_2CO}$] δ 1.74-1.77 (br, 12H, THF) (see ref. 7), 2.30 (s, 12H, $\mathrm{CH_3}$), 3.56-3.59 (m, 12H, THF), 7.11 (d, *J*= 8.1 Hz, 8H, Ar), 8.25 (d, *J*= 8.1 Hz, 8H); ^{13}C NMR [$\mathrm{(CD_3)_2CO}$] δ 21.6 ($\mathrm{CH_3}$), δ 26.3, 68.2 (THF), 125.8, 128.8, 143.4, 146.2 (Ar), 257.7 (C=S); UV/Vis (THF) λmax [nm] (log ε) 272 (5.39), 305 (5.08), 376 (4.78), 637 (3.91). Anal Found: C, 49.93; H, 5.10%. Calcd for $\mathrm{C_{44}H_{52}NaO_3S_8Sm}$: C, 49.92; H, 4.97%.

4 Single-crystallization solvents: THF/hexane = 4 : 2 for **2b**; 4 : 3 for **4**. Crystal data (Instrument: Rigaku AFC7R). **2b**: $\mathrm{C_{32}H_{37}O_5S_3Sm}$, 0.43 x 0.34 x 0.34 mm, monoclinic, *P*2$_1$/*n*, *a*=14.044(2), *b*=11.665(3), *c*= 20.218(3), *β*= 94.00(3), *V*= 3304.0(10) Å, Z= 4, *Dc* = 1.504 g/cm^3, *μ* (Mo, Kα), cm^{-1}= 20.08, Temp= -80 °C, *Rf*/*Rw*= 0.037/0.038, GOF= 1.60, No. of unique reflections= 7962. **4**: $\mathrm{C_{48}H_{60}NaO_4S_8Sm}$, 0.37 x 0.25 x 0.09, triclinic, *P*-1, *a*=15.596(8), *b*=16.128(4), *c*= 11.441(3), *α*=108.87(2), *β*=110.05(3), *γ*=79.31(3), *V*= 2632(1) Å, Z= 2, *Dc* = 1.427 g/cm^3, *μ* (Mo, Kα), cm^{-1}= 14.83, Temp= -80 °C, *Rf*/*Rw*= 0.048/0.049, GOF= 1.52. No. of unique reflections= 10986.

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9 Compounds **7~11** were comfirmed by comparison of the IR and ^{1}H and ^{13}C NMR spectra with those of the authentic samples which were previously prepared in this laboratory: **7** (R'= Me), IR (Neat): 1663 cm^{-1} (C=O); ^{1}H NMR ($\mathrm{CDCl_3}$): δ 2.40 (s, 3H, $\mathrm{CH_3}$), 2.46 (s, 3H, $\mathrm{SCH_3}$), 7.24 (d, *J*= 8.2 Hz, 2H, Ar), 7.86 (d, *J*= 8.2 Hz, 2H, Ar); ^{13}C NMR ($\mathrm{CDCl_3}$): δ 11.7 ($\mathrm{SCH_3}$), 21.7 ($\mathrm{CH_3}$), 127.2, 129.3, 134.6, 144.1 (Ar), 192.0 (C=O); **8**, IR (Neat): 1246 cm^{-1} (C=S); ^{1}H NMR ($\mathrm{CDCl_3}$): δ 2.36 (s, 3H, $\mathrm{CH_3}$), 2.75 (s, 3H, $\mathrm{SCH_3}$), 7.12 (d, *J*= 7.6 Hz, 2H, Ar), 7.93 (d, *J*= 7.6 Hz, 2H, Ar); ^{13}C NMR ($\mathrm{CDCl_3}$): δ 20.5 ($\mathrm{CH_3}$), 21.5 ($\mathrm{SCH_3}$), 126.8, 129.0, 142.6, 143.2 (Ar), 228.7 (C=S); MS (m/z): 182 ($\mathrm{M^+}$); **9**,[12] mp 88-89 °C; IR (KBr): 1710, 1670 cm^{-1}; **10**, dark blue oil, IR (Neat) 1688 cm^{-1} (C=O) (Lit.[13] 1690 cm^{-1}); ^{13}C NMR ($\mathrm{CDCl_3}$): δ 21.7 [*C*$\mathrm{H_3}$ (C=S)], 21.8 [*C*$\mathrm{H_3}$ (C=O)], 128.5-145.8 (Ar), 185.6 (C=O), 222.6 (C=S); **11**, mp 120-121 °C (Lit.[14] 109 °C), IR (KBr): 3240 (NH), 1651 (C=O) cm^{-1}, 1612 (NHC=O); ^{1}H NMR ($\mathrm{CDCl_3}$): δ 2.40 (s, 3H, $\mathrm{CH_3}$), 7.12 (t, *J*= 7.8 Hz, 2H, Ph), 7.23 (d, *J*= 7.7Hz, 2H, Ar), 7.33 (t *J*= 7.8 Hz, 2H, Ph), 7.63 (d, *J*= 7.8 Hz, 2H, Ar), 7.75 (d, *J*= 7.8 Hz, 2H, Ph), 7.99 (br, 1H, NH); ^{13}C NMR ($\mathrm{CDCl_3}$): δ 21.5 ($\mathrm{CH_3}$), 120.3, 124.4, 129.0, 129.3, 129.4, 132.1, 138.1, 142.3, (Ar), 165.8 (NHCO), 188 .7 (COS).

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