

Unexpected Synthetic Routes to Lanthanide Chalcogenido Clusters: $\text{Sm}_8\text{Se}_6(\text{SePh})_{12}(\text{THF})_8$ and $[\text{Sm}_7\text{S}_7(\text{SePh})_6(\text{DME})_7]^+$

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Received June 23, 1997

Inorganic clusters continue to attract considerable attention because they represent the bridge linking molecular and solid state chemistry and because they are useful tools for understanding the size-dependent physical properties of electronic materials.¹ While the metal chalcogenide (E, E = S, Se, Te) cluster chemistry of the main group² and transition metals³ is now firmly established, the analogous chemistry of the lanthanides (Ln) is virtually undeveloped. Structures of Ce_5Te_3 – $(\text{TeSi}(\text{SiMe}_3)_3)_9$ ⁴ and $(\text{C}_5\text{Me}_5)_2\text{Sm}_6\text{Se}_{11}$ ⁵ have been determined, but synthetic difficulties have inhibited systematic studies of structure–property relationships. The recent descriptions of molecular Ln chalcogenolate ($\text{Ln}(\text{ER})_x$; E = S, Se, Te; R = organic; $x = 2, 3$) complexes,⁶ coupled with the well-understood properties of $\text{LnE}_{x/2}$ solids, have set a foundation for interpreting the properties of cluster compounds. In this paper, we outline two new synthetic approaches to lanthanide chalcogenido (E, E = S, Se) clusters: C–Se bond cleavage by low-valent Ln and the reaction of $\text{Ln}(\text{SePh})_3$ with elemental S.

The conventional synthetic route to compounds containing Ln–chalcogenido bonds involves reduction of E or EPR_3 with a Ln(II) complex.⁷ Accordingly, we initially prepared green “ $\text{Sm}(\text{SePh})_2$ ”⁸ by reacting Sm with PhSeSePh in THF and then reacting the mixture with elemental Se. From this, deep orange crystals were obtained, and the air-sensitive product was identified as $\text{Sm}_8\text{Se}_6(\text{SePh})_{12}(\text{THF})_8$ (**1**) by low-temperature single-crystal X-ray diffraction.⁹ Cluster **1** (Figure 1) contains eight seven-coordinate Sm(III) ions at the vertices of a cube, while the Se^{2-} atoms cap each of the six faces. The 12 Se atoms from the SePh ligands each bridge one of the 12 edges,

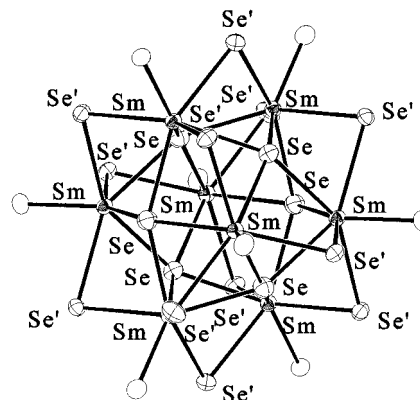


Figure 1. Molecular structure of $\text{Sm}_8\text{Se}_6(\text{SePh})_{12}(\text{THF})_8$ (**1**) with the C and H atoms removed and the O atom labels omitted for clarity. The Sm– Se^{2-} bond lengths range from 2.847(2) to 2.971(2) Å and average 2.93 Å, while the Sm–Se(Ph) (labeled Se') bond lengths range from 2.916(2) to 3.015(2) Å and average 2.98 Å. Thermal ellipsoids are shown at the 50% probability level.

and each metal atom is also coordinated to a THF ligand. The compound has a UV–vis absorption maximum in the visible spectrum at 341 nm, which is attributable to a ligand (SePh^- or Se^{2-}) to Sm(III) charge transfer.^{6b,c,g} Subsequent syntheses implicated “ $\text{Sm}(\text{SePh})_2$ ” as the source of Se^{2-} in **1**, and this was confirmed by preparing $\text{Sm}(\text{SePh})_2$ in THF and allowing the divalent compound to decompose thermally at room temperature. This chalcogen-free route¹⁰ gives the largest and cleanest yield of cluster **1**. While there are examples of $(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{II})$ cleaving C–O,¹¹ C–Sb,¹² or C–Bi¹³ bonds to yield molecular products, this is the first example of such reactivity in the less-reducing chalcogenolate compounds. Preliminary results suggest that the non-redox-active Ln will form similar cluster products.

While Ln clusters of the heavier chalcogens (Se ,⁵ Te)⁴ are rare, the corresponding sulfido clusters are unknown. Such clusters are particularly interesting as models for Ln ions doped into sulfide-based semiconductors¹⁴ and fiber optic materials.¹⁵ In the course of rationalizing heterometallic Ln/group 14 metal chalcogenolate structures,¹⁶ we found reference to thermochemical bond strengths¹⁷ that implied S would insert into Ln–Se bonds, which we thought could then lead to the preparation of

(1) For recent examples, see: (a) Alivisatos, A. P. *Science* **1996**, *271*, 933–7. (b) Brus, L. *Appl. Phys. A* **1991**, *53*, 465–74. (c) Steigerwald, M. L. *Polyhedron* **1994**, *13*, 1245. (d) Schaper, A. K.; Jiang, J.; Becker, J. A. *Adv. Mat.* **1997**, *9*, 343. (e) Empedocles, S. A.; Norris, D. J.; Bawendi, M. G. *Phys. Rev. Lett.* **1996**, *77*, 3873–6.

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(3) For example, see: (a) Brennan, J.; Siegrist, T.; Stuczynski, S.; Steigerwald, M. *J. Am. Chem. Soc.* **1992**, *114*, 10334–8. (b) Dahl, L. F.; Johnson, A.; Whoolery, S. *Inorg. Chim. Acta* **1994**, *227*, 269–83. (c) Fenske, D.; Fischer, A. *Angew. Chem.* **1995**, *34*, 307–9. (d) Mathur, P.; Sekar, P. *J. Chem. Soc., S Chem. Commun.* **1996**, 727–8.

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(8) Green Sm(II) chalcogenolates have precedence.^{6c}

(9) Compound **1** crystallizes in the orthorhombic space group *Pbca*, with $a = 26.099(7)$ Å, $b = 22.440(7)$ Å, $c = 20.002(5)$ Å, $V = 11714(6)$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 2.340$ g/cm³ (Mo K α radiation at -120 °C). Full-matrix least-squares refinement with 5226 unique observations [$F > 4\sigma(F)$] gave $R(F) = 0.046$ and $wR(F^2) = 0.092$. Complete crystallographic details are given in the Supporting Information.

(10) Synthesis of **1**: Under nitrogen, PhSeSePh (recrystallized from hexane; 1.26 g, 4.0 mmol) was added to a Schlenk tube containing Sm powder (0.62 g, 4.1 mmol), Hg (0.050 g, 0.25 mmol), and THF (50 mL). After 1 day, a brown solution with a green precipitate was observed. After 7 days the reaction was filtered, concentrated to 25 mL, and layered with hexane to give orange crystals (90 mg, 5% based on Se) that lose THF and become amorphous within hours of isolation. The compound did not melt but turned darker orange around 140 °C and continued to darken with increasing temperature. Anal. Calcd for $\text{C}_{104}\text{H}_{124}\text{O}_8\text{Se}_8\text{Sm}_8$: C, 30.3; H, 3.03. Found: C, 28.5; H, 2.80. IR (Nujol): 2925 (s), 2855 (s), 1571 (w), 1460 (s), 1378 (s), 1262 (w), 1056 (w), 1020 (w), 857 (m), 732 (s), 692 (m), 662 (m), 465 (m) cm⁻¹. In the ¹H NMR spectrum (3 mg in NC_5D_5 , 20 °C), only the displaced THF protons (3.64, 1.58) were observed. λ_{max} (THF) = 341 nm.

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chalcogen-rich reagents for subsequent cluster syntheses. Slow addition of sulfur to $\text{Sm}(\text{SePh})_3$ ¹⁸ (prepared by reducing Ph_2Se_2 with Sm/Hg amalgam) in dimethoxyethane (DME) dissolved the precipitate, and the orange solution turned light yellow, before a yellow solid precipitated. When less than a full equivalent of S was added,¹⁹ light yellow air-sensitive crystals of $[\text{Sm}_7\text{S}_7(\text{SePh})_6(\text{DME})_7][\text{Hg}_3(\text{SePh})_7]\cdot\text{DME}$ (**2**) were isolated and characterized by low-temperature single-crystal X-ray diffraction (Figure 2).²⁰ The six seven-coordinate and one eight-coordinate $\text{Sm}(\text{III})$ ($\text{Sm}3$) ions in cluster **2** form two square pyramids that share one Sm_3 face with four $\mu_3\text{-S}^{2-}$ (S1, S4, S6, S7) and two $\mu_5\text{-S}^{2-}$ (S2, S5) capping the external faces of the cluster, and one $\mu_4\text{-S}^{2-}$ (S3) bridging two reentrant Sm_3 faces. Each Sm coordination sphere is saturated with a chelating DME ligand. The $\text{Hg}_3(\text{SePh})_7$ anion has no structural precedent, but SePh abstraction from Ln by $\text{Hg}(\text{SePh})_2$ has been noted previously.^{16,21} In contrast to **1**, the visible spectrum of **2** is

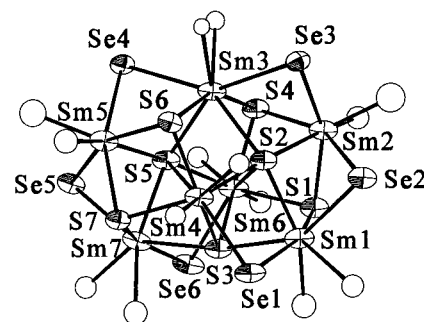


Figure 2. Molecular structure of the cation in $[\text{Sm}_7\text{S}_7(\text{SePh})_6(\text{DME})_7]^+[\text{Hg}_3(\text{SePh})_7]^-$ (**2**) with the C and H atoms removed and the O atom labels omitted for clarity. The Sm–S bond lengths range from 2.66(2) to 2.93(2) Å (average 2.79 Å), and the Sm–Se bond lengths range from 2.930(9) to 3.12(1) Å and average 3.03 Å. Long “bonds” (3.4 Å) from $\text{Sm}4\text{--}S5$ and $\text{Sm}6\text{--}S2$ are also included in the figure. Thermal ellipsoids are shown at the 50% probability level.

featureless, which suggests that the visible absorption in **1** results from a Se^{2-} to $\text{Sm}(\text{III})$ charge transfer. Chalcogenido displacement of chalcogenolate appears to be a general reaction: both the redox inactive Ln^{2+} chalcogenolates and more covalent metal selenolates (i.e. $\text{Hg}(\text{SePh})_2$)²³ react similarly.

Acknowledgment. This work was supported by the National Science Foundation under grant no. CHE-9628834.

Supporting Information Available: Complete tables of crystallographic details, bond geometries, and fully labeled ORTEP diagrams for **1** and **2** (30 pages). Structure factor tables are available from the authors upon request. See any current masthead page for ordering and Internet access instructions.

JA972059K

(20) Compound **2** crystallizes in the triclinic space group $P\bar{1}$, with $a = 16.853(7)$ Å, $b = 17.642(9)$ Å, $c = 26.810(12)$ Å, $\alpha = 107.28(4)^\circ$, $\beta = 98.14(4)^\circ$, $\gamma = 105.67(4)^\circ$, $V = 7112(6)$ Å³, $Z = 2$, $\rho_{\text{calcd}} = 2.161$ g/cm^{−3} (Mo $K\alpha$ at -120 °C). Full-matrix-block least-squares refinement with 4364 unique observations [$F > 4\sigma(F)$] gave $R(F) = 0.108$ and $wR(F^2) = 0.240$. Complete crystallographic details are given in the Supporting Information.

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(17) (a) Bond strengths in diatomic molecules (in kcal/mol): SmS (93),^{17b} SmSe (79.1 ± 3.5),^{17c} S–S (101.65),^{17d} S–Se (88.7 ± 1.6).^{17e} (b) Fenochka, B. V.; Gorkienko, S. P. *Zh. Fiz. Khim.* **1973**, *47*, 2445. (c) Nagai, S.; Shinmei, M.; Yokokawa, T. *J. Inorg. Nucl. Chem.* **1974**, *36*, 1904–5. (d) Hubert, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure Constants of Diatomic Molecules*; Van Nostrand: New York, 1979. (e) Drowart, J.; Smoes, S. *J. Chem. Soc., Faraday Trans.* **1977**, *73*, 1755–67.

(18) Sm reacts with $3/2\text{PhSeSePh}$ to give $\text{Sm}(\text{SePh})_3$ quantitatively. The red product is very soluble in THF ($\lambda_{\text{max}} = 409$ nm), but only slightly soluble in DME. See: Jongseong Lee, Ph.D. Thesis, Rutgers University, October 1996.

(19) Synthesis of **2**: PhSeSePh (0.94 g, 3.0 mmol) was added to a Schlenk tube containing Sm (0.30 g, 2.0 mmol), Hg (0.15 g, 0.75 mmol), and DME (50 mL). After 1 day a yellow precipitate had formed. After 2 days S was added (48 mg, 1.5 mmol) and the precipitate dissolved within 30 min. The reaction was stirred for an additional 1 day, after which the yellow solution was filtered, concentrated to about 25 mL, and layered with hexane (25 mL) to give pale yellow crystals (75 mg, 8%). The compound did not melt but turned golden around 240 °C and continued to darken with increasing temperature. Anal. Calcd for $\text{C}_{110}\text{H}_{145}\text{O}_{16}\text{Hg}_3\text{S}_7\text{Se}_{13}\text{Sm}_7$: C, 28.0; H, 3.00. Found: C, 26.8; H, 3.05. The compound does not show an optical absorption maximum from 300 to 800 nm in THF. IR (Nujol): 2929 (s), 1571 (m), 1461 (s), 1378 (s), 1261 (w), 1190 (w), 1113 (w), 1095 (w), 1044 (w), 857 (s), 823 (w), 807 (w), 732 (s), 690 (s), 664 (m), 464 (s) cm^{-1} . NMR (NC_5D_5 , 20 °C): δ 7.95 (14 H), 7.05 (21 H), 3.48 (32 H), 3.25 (48 H) (the Sm–SePh resonances were not observed).