Heterometallic Rare Earth/Group II Metal Chalcogenolate Clusters

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Heterometallic Group II/rare earth (RE) thiolates, selenolates, and tellurolates have a broad range of potential applications in the rapidly developing field of RE-doped semiconductor technology.[1-2] In addition to the obvious utility of these compounds to deliver controlled levels of RE chalcogenide into II–VI semiconductor lattices, these compounds are also potential precursors to new forms of RE-doped semiconductors, much as transition-metal chalcogenolate precursors[3] have been used to prepare nanocluster[3d] and metastable solid-state metal chalcogenides.[3e] Further, heterometallic RE/Group II chalcogenolates can serve as models for understanding the structural perturbations and photoluminescent properties associated with RE ions in a covalent semiconductor matrix. Given the tendency of RE chalcogenolates[4] to form polymetallic species[4c–f] with bridging chalcogenolate ligands, we reasoned that RE complexes of the heavier chalcogenolates could be stabilized by bridging the chalcogenide to a softer Group II metal to form heterometallic compounds. In this paper, we show that such stabilization is significant, and we describe the isolation and structural characterization of the first two examples of a broad class of heterometallic chalcogenolate complexes having the general formula $MM'(EPh)_x(L)_y$ [M = Zn, Cd, Hg; M′ = divalent (x = 4) or trivalent (x = 5) rare earth; E = S, Se, Te; L = THF, pyridine].

Initially, we sought to establish whether $Hg(SePh)_2$ coordination would stabilize $Eu(SePh)_3$, which is unstable[4d] with respect to the formation of $Eu(SePh)_2$ and Ph_2Se_2. The reaction of 2.5 equiv of diphenyl diselenide with europium/mercury amalgam proceeds rapidly at room temperature to give a yellow solid that can be isolated by filtration and crystallization.[5] Spectroscopic characterization of the product revealed little structural information; the ^{1}H NMR spectrum contained only a single set of broad ($w_{1/2}$ = 50–80 Hz) Ph and THF resonances. The visible spectrum contained no absorption maximum from 300–800 nm. For unambiguous structural assignment, the product was examined by single crystal X-ray diffraction[6] and shown to be the tetrametallic chalcogenolate $[(THF)_3Eu(\mu_2\text{-}SePh)_2(\mu_3\text{-}SePh)Hg(SePh)]_2\cdot 2THF$ (**1**). The structure of **1** (Figure 1a) contains

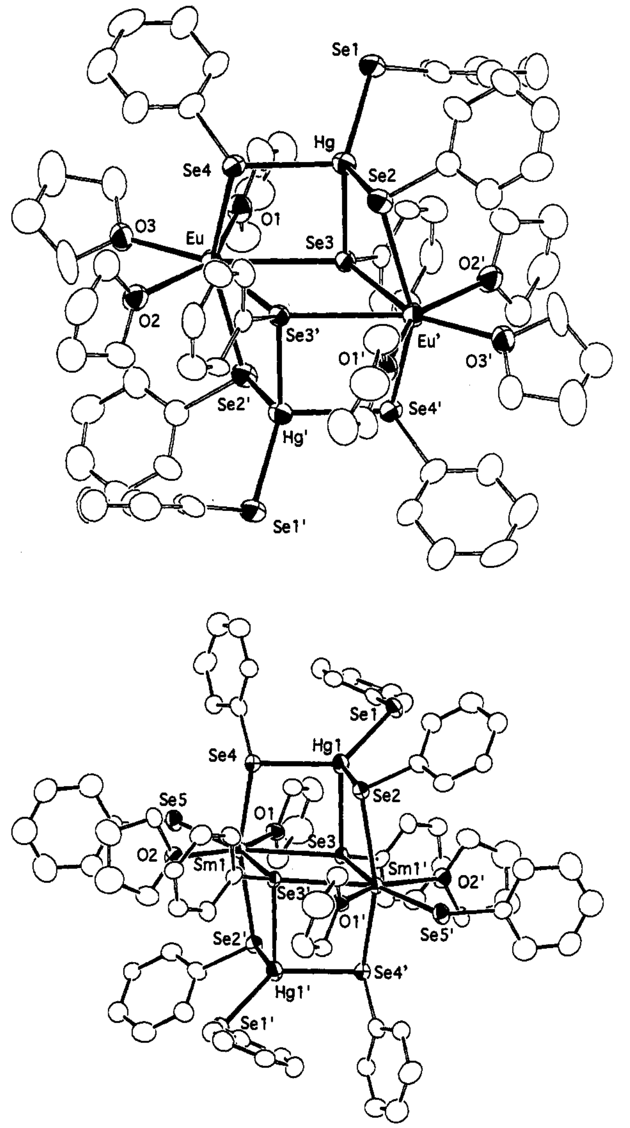

Figure 1. (a, top) Molecular structure of the the tetrametallic chalcogenolate cluster $[(THF)_3Eu(\mu_2\text{-}SePh)_2(\mu_3\text{-}SePh)Hg(SePh)]_2\cdot 2THF$ (**1**). The tetrametallic framework is connected by μ_2 and μ_3 phenyl selenolates, with a terminal phenyl selenolate bound to the the mercury and three THF ligands coordinating to the Eu ion. Significant bond lengths (Å): Hg–Se(1), 2.555(1); Hg–Se(2), 2.731(1); Hg–Se(3), 2.675(1); Hg–Se(4), 2.760(1); Eu–Se (2′), 3.111(1); Eu–Se (3), 3.232(1); Eu–Se (3′), 3.226(1); Eu–Se (4), 3.085(1); Eu–O(1), 2.567(7); Eu–O(2), 2.555(7); Eu–O(3), 2.560(7). Significant bond angles (deg): Se(1)–Hg–Se(4), 110.38(4); Se(1)–Hg–Se(2), 117.98(4); Se(4)–Hg–Se(2), 93.82(4); Se(1)–Hg–Se(3), 113.98(4); Se(4)–Hg–Se(3), 96.47(4); Se(2)–Hg–Se(3), 95.78(4). (b, bottom) Molecular structure of $[(THF)_2Sm(SePh)(\mu_2\text{-}SePh)_2(\mu_3\text{-}SePh)Hg(SePh)]_2$ (**2**). Cluster **2** has the same cluster framework as **1**, with the central THF ligand in **1** replaced by a terminal phenyl selenolato ligand in **2**. In the structure there are two independent molecules that differ in the orientation of the phenyl substituents. Significant bond lengths (Å): Hg(1)–Se(1), 2.551(2); Hg(1)–Se(2), 2.690(2); Hg(1)–Se(3), 2.916(2); Hg(1)–Se(4), 2.609(2); Sm(1)–Se(2′), 2.976(2); Sm(1)–Se(3), 3.077(2); Sm(1)–Se (3′), 3.100(2); Sm(1)–Se(4), 3.015(2); Sm(1)–Se(5), 2.859(2); Sm(1)–O(1), 2.40(1); Sm(1)–O(2), 2.40(1). Significant bond angles (deg): Se(1)–Hg(1)–Se(4), 128.96(6); Se(1)–Hg(1)–Se(2), 114.50(6); Se(4)–Hg(1)–Se(2), 103.16(6); Se(1)–Hg(1)–Se(3), 119.77(6); Se(4)–Hg(1)–Se(3), 90.64(6); Se(2)–Hg(1)–Se(3), 91.96(6).

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a pair of four-coordinate Hg ions, each having one terminal phenyl selenolate ligand, and each bridged to a pair of seven-coordinate Eu(II) ions by two μ_2 and one μ_3 phenyl selenolates. The Eu geometry is similar to the Eu geometry in the one-dimensional polymer $[(THF)_3Eu(SePh)_2]_n$ (**3**).[4d] From the statistically equivalent Eu–O bond lengths in **1** and **3** and slightly longer (0.04 Å) Eu–Se bond lengths to the μ_2-SePh ligands in **1** relative to **3**, we can conclude that the Hg(II) ion does little to perturb the bonding to the rare earth. The Hg-μ_2-Se bond lengths are similar to literature values of structurally related compounds,[7] but, in contrast to the Eu–Se bonds, they they do not simply increase as a function Se coordination number—in **1**, the Hg-μ_3-Se(3) bond is shorter than either of the Hg-μ_2-Se bonds.

To establish whether trivalent rare earths would also form Group II/RE heterometallic chalcogenolates, we began working with Sm, the most reducing of the redox active rare earths. The reduction of diphenyl diselenide with Hg/Sm in THF gives a red solution from which an orange crystalline solid can be crystallized.[8] Spectroscopic characterization again gave little structural information, other than to indicate that no monometallic products had been isolated, and so the compound was studied by single crystal X-ray diffraction[9] and shown to be $[(THF)_2Sm(SePh)(\mu_2\text{-}SePh)_2(\mu_3\text{-}SePh)Hg(SePh)]_2$ (**2**). The structure of **2** (Figure 1b) contains the same tetrametallic framework as **1**, with the central THF ligand replaced by a terminal phenyl selenolate. There are two molecules in the unit cell that differ primarily in the orientation of the phenyl groups. The M–O bond lengths in trivalent **2** are shorter by 0.16 Å and the M–Se bond lengths by 0.10 Å than the related bonds in divalent **1**. Bonds to the mercury ion differ significantly within the two structures. In both compounds the Hg is distorted significantly from ideal tetrahedral geometry, but the deviation is greater in **2**, which has a broader range of Hg–Se distances. The terminal Hg–Se bonds in **1** and **2** are statistically equivalent, but there are significant perturbations in the Hg bonds to the bridging selenolates—both of the Hg-μ_2-Se bonds in **2** are considerably shorter than the related bonds in **1**, while the Hg-μ_3-Se bond in **2** is considerably longer than the Hg-μ_3-Se bond in **1**.

Compounds **1** and **2** demonstrate that both divalent and trivalent rare earth chalcogenolates form stable heterometallic complexes with Group II chalcogenolates. From the absence of UV–visible absorptions characteristic of monometallic products, we can conclude that **1** and **2** retain some form of heterometallic structure in donor solvents as basic as pyridine. The ^1H NMR spectra of **1** and **2** show only a single, broad set of phenyl selenolate resonances, indicating that the molecules are fluxional. Preliminary data on analogous Zn, Cd, S, and Te derivatives indicate that this is an extremely general class of heterometallic compounds and that they will be useful in the low-temperature synthesis of ternary solid-state chalcogenides.

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Supplementary Material Available: Tables of crystallographic details, additional bond geometries, and complete ORTEP diagrams for **1** and **2** (26 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information. Structure factor tables are available from the authors.

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(5) All synthetic work was carried out using conventional Schlenk techniques in a nitrogen atmosphere. Synthesis of **1**: diphenyl diselenide (2.25 g, 7.2 mmol) was dissolved in THF (60 mL) and added to a Schlenk tube containing europium (0.55 g, 3.6 mmol) and an excess of mercury (2.5 g, 12.5 mmol). After 2 h, a yellow precipitate began to form. After 4 days, the mixture was heated to reflux until the product dissolved, the yellow solution was filtered while hot, and a yellow crystalline product (3.0 g, 66%) formed upon cooling the filtrate to room temperature. The compound did not melt but turned opaque and orange around 64 °C, eliminated a gas around 140 °C, turned green at 230 °C and deep red at 320 °C. The compound lost the THF of solvation within minutes of isolation. Anal. Calcd for $C_{36}H_{44}O_3EuHgSe_4$: C, 36.2; H, 3.70. Found: C, 35.5; H, 3.65. The compound did not show an optical absorption maximum from 300 to 800 nm in either THF or pyridine. IR (Nujol): 2927 (s), 2855 (s), 1572 (w), 1467 (s), 1378 (s),1261 (w), 1068 (w), 1021 (w), 873 (w), 800 (w), 732 (w), 692 (w), 666 (w), 465 (w) cm^{-1}. ^1H NMR (CD_3CN, 20 °C): 7.25 (2H, $w_{1/2} = 80$ Hz), 6.85 (3H, $w_{1/2} = 100$ Hz), 3.63 (4H, $w_{1/2} = 50$ Hz), 1.73 (4H, $w_{1/2} = 20$ Hz).

(6) **1** crystallizes in the monoclinic space group $P2_1/c$, with $a = 13.973(2)$ Å, $b = 16.567(2)$ Å, and $c = 18.340(3)$ Å, $\beta = 95.08(2)°$, $V = 4229(1)$ Å^3, $Z = 4$, $\rho_{calc} = 1.987$ Mg/m^{-3}, (Mo Kα radiation at 190 K). Full-matrix least-squares refinement with 3291 unique observations $[F > 4\sigma(F)]$ gave $R(F) = 0.037$, $R_w(F^2) = 0.080$. Complete crystallographic details are given in the supplementary material.

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(8) Synthesis of **2**: THF (50 mL) was added to a mixture of mercury (4.6 g, 22.9 mmol), samarium powder (0.45 g, 3 mmol), and diphenyl diselenide (2.35 g, 7.5 mmol). The solution quickly turned red and, after four days, was filtered and concentrated to 20 mL. Layering the red solution with diethyl ether (70 mL) gave large orange crystals (3.5 g, 91%; mp 137 °C with gas evolution, dec 272 °C) that were isolated immediately prior to characterization. Anal. Calcd for $C_{38}H_{41}O_2HgSe_5Sm$: C, 35.8; H, 3.25. Found: C, 36.1; H, 3.45. The compound did not show an optical absorption maximum from 300 to 800 nm in either THF or pyridine. IR (Nujol): 2927 (s), 2855 (s), 1572 (w), 1467 (s), 1378 (s), 1261 (w), 1068 (w), 1021 (w), 873 (w), 800 (w), 732 (w), 692 (w), 666 (w), 465 (w) cm^{-1}. ^1H NMR (CD_3CN, 20 °C): 7.33 (10H, $w_{1/2} = 70$ Hz), 6.95 (15H, $w_{1/2} = 50$ Hz), 3.63 (8H, $w_{1/2} = 10$ Hz), 1.81 (8H, $w_{1/2} = 8$ Hz).

(9) **2** crystallizes in the monoclinic space group $P2_1/c$, with $a = 15.834(9)$ Å, $b = 23.272(4)$ Å, and $c = 21.431(9)$ Å, $\beta = 100.67(4)°$, $V = 7761(6)$ Å^3, $Z = 4$, $\rho_{calc} = 2.183$ Mg/m^{-3} (Mo Kα radiation at 155 K). Full-matrix least-squares refinement with 5874 unique observations $[F > 4\sigma(F)]$ gave $R(F) = 0.053$, $R_w(F^2) = 0.099$. Complete crystallographic details are given in the supplementary material.