Lanthanide Clusters with Internal Ln Ions: Highly Emissive Molecules with Solid-State Cores

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Abstract: “Er(SePh)2S6I6” reacts with elemental S to give (THF)10Er6S6I6, a double cubane cluster with one face of the Er6S6 cube capped by an additional Er6S6. Reactions with a mixture of elemental S/Se results in the formation of (THF)14Er10S6(Se2)6I6, a cluster composed of an Er6S6 double cubane core, with two “Er2(Se2)6” units condensed onto opposing rectangular sides of the Er6S6 fragment. This deposition of Er6S6 totally encapsulates the two central Er with chalcogen atoms (4 S, 4 Se) and excludes neutral THF donors or iodides from the two primary coordination spheres. The Er10 compound is the first lanthanide to contain internal, chalcogen encapsulated Ln. This cluster shows strong fluorescence at 1544 nm with a measured decay time of 3 ms and an estimated quantum efficiency of 78%, which is comparable to Er doped solid-state materials. The unusual fluorescence spectral properties of (THF)14Er10S6Se12I6 are unprecedented for a molecular Er complex and are attributed to the low phonon energy host environment provided by the I−, S2−, and Se2− ligands.

Introduction

Extraordinary developments in transition metal cluster chemistry have provided considerable insight into the size-dependent physical properties of quantum-confined systems.1–3 Synthetic studies with these covalent metals (M = Zn, Cd, Hg, Cu, Ag,...) have produced extremely large metal chalcogenido (E, E = S, Se, Te) cluster compounds with precisely defined cluster surfaces and internal, chalcogenido-encapsulated M.4–8 Most of these internal M have coordination environments that resemble the environments found in bulk solid-state materials. With both molecular and solid-state characteristics, these clusters represent a unique opportunity to develop novel materials with superior physical properties.

The analogous cluster chemistry of the lanthanides (Ln) is considerably less developed.9–20 Ionic Ln form comparatively unstable (i.e., heat, water, oxygen, and light sensitive) compounds with S, Se, and Te, and these experimental complications tend to inhibit progress within the field. One particularly general synthetic approach to Ln clusters with chalcogenido anions involves reduction of elemental E by the chalcogenolates ligands in Ln(EPh).19–21

Common to all isolable LnE, clusters is the coordination of at least one ancillary ligand to each Ln in a compound, a feature that contrasts dramatically with abundance of internal, chalcogen encapsulated M. In most LnE compounds, these ancillary ligands are neutral Lewis bases (i.e., THF, pyridine, DME) and or X− (X = EPh, I). Similarly, in the limited series of organometallic lanthanide chalcogen cluster compounds,15,19 every Ln coordinates to a relatively electronegative Cp ligand. The tendency of Ln to avoid encapsulation by these electropositive E ligands is consistent with the view of these metals as oxophilic, but even with oxo ligands,21–25 Ln cluster...
chemistry has yet to reach the level of achievement set by main group and transition metal chemists.

As one of the most interesting fundamental goals of cluster chemistry is to study the evolution of physical properties along the pathway connecting molecules, clusters, and solid-state compounds, it is important to be able to prepare increasingly larger cluster compounds with both surface and internal Ln. Such products are expected to exhibit unprecedented chemical or physical properties, optimally incorporating the key advantages of molecular and solid-state materials.

In the lanthanide domain, one ideal combination of molecular and solid-state physical properties would unite the emission properties of solid-state Ln materials with the solubility properties of molecular compounds. Er(III) has an emission at 1.54 µm that has extensive applications in optical fiber signal amplification.6–10 While this emission has been studied extensively in solid-state materials (e.g., halides, chalcogenides, and oxides), the ability to stimulate emission from molecular Er sources has been hampered by the accompanying high phonon energies of hydrocarbon- or hydroxide-based coordination spheres, which can easily bridge the energy transitions desired for erbium and thus nonradiatively quench emission.11–16 Thus, the short lifetimes and low intensities of these compounds have lessened interest in these molecular complexes. Soluble, molecular compounds with a coordination environment similar to those provided by solid-state materials could be useful for delivering emissive Er ions into less conventional matrices.

Outlined here is a heterochalcogen approach to the synthesis of increasingly large cluster compounds. Using a lanthanide sulfido cluster as a nucleation site, Ln₂(S₂)₃ fragments are attached to the sides of the sulfido core, generating a larger cluster with internal, chalcogen encapsulated lanthanide ions. The emission properties of this material are compared with related molecular and solid-state materials.

**Experimental Section**

**General Methods.** All syntheses were carried out under ultrapure nitrogen (JWS), using conventional drybox or Schlenk techniques. Solvents (Fisher) were refluxed continuously over molten alkali metals or K/benzophenone and were collected immediately prior to use. Anhydrous pyridine (Aldrich) was purchased and refluxed over KOH. Er was purchased from Strem. PhSeSePh was purchased from Aldrich. Anhydrous pyridine (Aldrich) was purchased and refluxed over KOH.

**X-ray Structure Determination of 1 and 2.** Data for 1 and 2 were collected on a Bruker Smart APEX CCD diffractometer with graphite monochromated Mo Kα radiation (λ = 0.710 73 Å) at 100 K. The data were corrected for Lorentz effects, polarization, and absorption, the latter by a multiscan (SADABS) method. The structures were solved by Patterson methods (SHELX86).29 All–none hydrogen atoms were refined (SHELXL97)29 based upon Fobs.2 All hydrogen atom coordinates were calculated with idealized geometries (SHELXL97). Scattering factors (f0, f1, f2) are as described in SHELXL97. Crystallographic data and final R indices for 1 and 2 are given in Table 1. ORTEP drawings40 for 1 and 2 are shown in Figures 1 and 2, respectively, while color representations of the core atoms for 1 and 2 are given in Figure 3. Significant bond geometries for 1 and 2 are given in the figure captions. Complete crystallographic details for 1 and 2 are given in the Supporting Information.

**Optical Properties.** The infrared emission spectra were recorded by exciting the sample with a 980 nm band of a laser diode in the 45° excitation geometry. Emission from the sample was focused onto a 1 mm monochromator (Jobin Yvon, Triax 550, Edison, NJ) and detected by a thermoelectrically cooled InGaAs detector (EO Systems, Phoenixville, PA). The signal was intensified with a lock-in amplifier (Stanford Research System, SR 850 DSP, Sunnyvale, CA) and processed by computer using Spectramax software (GRAMS 32, Salem, NH). The
Results

The sulfido cluster (THF)$_{10}$Er$_6$S$_6$I$_6$ (1) is isolated from the reaction of “Er(I)SePh$_2$” with elemental S in THF at room temperature (reaction 1). The compound exhibits the characteristic light pink color of Er(III) and is soluble in THF or pyridine. Structural analysis of this compound reveals a double cubane framework, with one face of an Er$_4$S$_4$ cubane cluster capped by an additional Er$_2$S$_2$ layer. Figure 1 shows an ORTEP diagram of 1, and the figure caption gives a listing of significant bond lengths and angles for the compound. There are single terminal iodides coordinated to all six Er, and the remaining octahedral coordination sites are saturated with THF ligands.

Figure 1. ORTEP diagram of the double cubane cluster (THF)$_{10}$Er$_6$S$_6$I$_6$ with thermal ellipsoids are drawn at the 50% probability level, the oxygen atoms unlabeled, and the C and H atoms removed for clarity. Significant distances (Å) and angles (deg) for atoms unlabeled, and the C and H atoms removed for clarity. Significant geometries about the Ln are nearly octahedral, and Er octahedral coordination sites are saturated with THF ligands. Bond lengths appear to have a directional dependence, with Er bonds trans to I consistently longer than related bonds trans to other atoms: –x + 1, y, –z + 1/2.

Increasing the starting ratio of Ln/I and adding a mixture of S/Se results in the formation of (THF)$_{14}$Er$_{10}$S$_6$(Se$_2$)$_6$I$_6$ (reaction 2). A low-temperature single-crystal X-ray diffraction analysis of 2 was obtained, and an ORTEP diagram for 2 is given in Figure 2, with significant bond lengths and angles given in the Supporting Information.

Figure 2. Molecular structure of the decanuclear heterochalcogen cluster 2 with the thermal ellipsoids drawn at the 50% probability level, the oxygen atoms unlabeled, and the C and H atoms removed for clarity. Significant distances (Å) for 2: Er(1)–S(1), 2.781(4); Er(1)–S(4)$^\prime$, 2.814(4); Er(1)–S(2), 2.834(4); Er(1)–S(3), 2.866(4); Er(1)–Se(6), 2.907(2); Er(1)–Se(3), 2.933(2); Er(1)–Se(1), 3.013(2); Er(1)–Se(5), 3.047(19); Er(2)–O(1), 2.333(13); Er(2)–S(4), 2.662(5); Er(2)–S(2), 2.677(10); Er(2)–Se(1), 2.723(5); Er(2)–Se(2), 2.823(2); Er(2)–I(1), 2.998(16); Er(3)–O(2), 2.294(12); Er(3)–O(3), 2.301(11); Er(3)–S(3), 2.594(12); Er(3)–S(1)$^\prime$, 2.664(5); Er(3)–S(4)$^\prime$, 2.676(5); Er(3)–Se(4), 2.833(2); Er(4)–O(5), 2.344(13); Er(4)–O(4), 2.343(14); Er(4)–S(4)$^\prime$, 2.676(5); Er(4)–Se(3), 2.785(2); Er(4)–Se(4), 2.887(2); Er(4)–Se(6), 2.961(2); Er(4)–I(3), 3.037(16); Er(5)–O(6), 2.300(14); Er(5)–O(7), 2.359(13); Er(5)–S(1), 2.671(14); Er(5)–Se(1), 2.769(2); Er(5)–Se(2), 2.903(2); Er(5)–Se(5), 2.906(2); Er(5)–I(2), 3.045(18). Symmetry transformations used to generate equivalent atoms: –x + 1, y, –z + 1/2.
the length of the Er6S6 cube are now 169.6
lengths found in J. Appl. Phys
J. AM. CHEM. SOC. 9 (41) Schlaich, H.; Lindner, G.-G.; Feldmann, J.; Göbel, E. O.; Reinen, D. I13/2
framework upon coordination of the two Er2(Se2)3 units. At the
Figure 4. Absorption spectrum of (THF)14Er10S6Se12I6 with standard
Figure 5. Comparison of the emission spectrum of Er3+ in (THF)14Er10S6
Center:
Table 2. Comparison of the Fluorescence Spectral Data of
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procedure43,44 a quantum efficiency of 78% is obtained for 2. Both
time and quantum efficiency values represent averages for all Er in the cluster. The fluorescence spectral width (fwhm) and stimulated emission cross-section are estimated to be, respectively, 61 nm and 4.1 × 10⁻⁻²¹ cm², which are comparable to the well-known host LaF₃/Er (Table 2).42 With 61 and 1542 nm, an available optical bandwidth of 7.5 THz is obtained.

Discussion

Cluster 2 is yellow because of a localized electronic excitation on the diselenide ligand41 that masks the characteristic Er color. Representative absorption and emission spectra of 2 are shown in Figures 4 and 5, respectively. The emission spectrum of Er-doped LaF₃ nanocrystals having comparable Er concentration is shown for comparative purposes.42 The pump photons at 980 nm populate the 4I15/2 excited state. A part of the excited population decays to 4I13/2 by multiphonon relaxation, and the remaining population will appear as radiative decay by the 4I13/2 channel, which is responsible for the 1542 nm emission. The lifetime of this emission was extracted from an exponential curve fit of the 1542 nm fluorescence decay (see Supporting Information) with a value of 3 ms. With this fluorescence decay time the quantum yield of 1542 nm emission can be estimated from the ratio of the fluorescence decay time (τf) to radiative or “natural” decay time (τr). With a calculated radiative decay time of 3.85 ms following the Judd–Ofelt

produced compounds with at least one more electronegative donor atom included within the primary Ln coordination sphere. Of the chalcogenido clusters in the literature, only the base free tellurolate decomposition product[26] Ce₂Te₂(TeSi(SiMe₃)₃)₄ has been described, and the transient nature of this product unfortunately precluded detailed characterization. In all the isolable chalcogenido clusters, every Ln has been bound to at least one THF, DME, or pyridine ligand.

Cluster 2 also contains S²⁻ ligands that can be described as internal, rather than surface atoms. Chalcogen “encapsulation” by Ln is also uncommon but has been noted in the structure of (DME)₇Nd₆Sr(SePh)₁₂[43],[44] which contained a single μ₃-sulfido ligand in a tetragonal pyramidal geometry. Organometallic clusters have also contained Ln encapsulated Se²⁻, in both Cp₆Sm₂Se₁₁[45] and the ionic clusters[46] Na[TFS][Cp₆]Sm₂Se₁₁ and [Li(TFS)]₂[Cp₆Nd₂Se₁₃], where central μ₂Se²⁻ ligands are enveloped by an octahedral array of Ln(III), an environment found in solid-state LnE (NaCl)[47,48].

With internal E²⁻ and Ln, 2 can be compared with solid-state LnE materials. Geometries about the internal S²⁻ in 2 are not as ideal as the internal octahedral E²⁻ in the organometallic derivatives, and they also have lower coordination numbers than S²⁻ ions in solids, i.e., Tm₃S₅[50,51] where the five-coordinate S have Tm–S–Tm angles that resemble a tetragonal pyramid. Similarly, the two eight-coordinate encapsulated Er(1) have the highest CN in the cluster; yet these are still not as high as the CN in the monocapped square antiprisms found in the structure of H₂O₃Se₅[52]. It is worth noting that, in contrast, geometries about both S and Se in the group 12 MS clusters are all ideal tetrahedra,[6] just as they are in binary solid-state MS compounds.

The chalcogen atoms in 2 are surprisingly ordered. Random arrays of S and Se in heterochalcogen materials have considerable literature precedent,[53,54] but the internal nature of the E²⁻ ligands in the present system, coupled with the difference in formal oxidation state, gives a structure with compositionally ordered S²⁻ and (Se₂)²⁻ ligands for the chemically distinct sites and no evidence to suggest the presence of Se²⁻ or (SSe)²⁻.

The optical properties also reflect the structural arguments indicating Er is bonded in an environment where S, Se, and I are its nearest neighbors. The reported 3 ms emission lifetime is typical of a low phonon energy host, which is supported by Table 3 where the emission lifetimes of various classes of low phonon energy hosts are summarized and found to range from 2.3 to 30 ms. More specifically, Er ions encapsulated by selenide, sulfide, or iodide have lifetimes that range from 2.3 to 4 ms.[26–8] In contrast, molecular complexes of Er typically exhibit lifetime data in the microsecond range,[31–6] which are characteristic of high phonon energy materials.

In Er³⁺ compounds one of the principal channels of multi-phonon nonradiative decay is via 4I₁₁/₂→4I₁₃/₂, which is in the frequency region of 3700 cm⁻¹. This nonradiative channel can reduce the effective population density at 4I₁₁/₂ and hence the fluorescence decay time and efficiency of the 1540 nm emission. Similarly the population of the 4I₁₁/₂ state during the 4I₁₁/₂→4I₃/₂ decay can be further lost by vibrational groups of frequency 6500 cm⁻¹. If Er³⁺ is directly attached to any of these vibrational groups or its harmonics, higher nonradiative loss can be expected with low quantum efficiency as observed in all molecular Er complexes reported to date. In most of the molecular complexes the two main vibrational groups quenching the fluorescence efficiency of Er³⁺ are C–H and O–H. The second-order vibrational energy of C–H (2960 cm⁻¹) is resonant with the Er³⁺ first excited state (6500 cm⁻¹). Similarly O–H is one of the potential quenchers of Er luminescence, because its first vibrational overtone (3400 cm⁻¹) is strongly resonant with the 4I₁₁/₂→4I₃/₂ transition (6500 cm⁻¹). Cluster 2 has a complete absence of C–H or O–H vibrational groups in the core, and the CH groups from the THF ligands are distantly connected to Er through a relatively weak dative bond.

The low phonon nature of 2 also explains why the estimated quantum efficiency value of 78% is so high, in fact the highest value reported for a molecular compound containing Er. When comparing the fluorescence spectral width (fwhm) and stimulated emission cross section to those of other low phonon energy hosts such as LaF₃/Er,[42] similar values are obtained (Table 2). The radiative quantum efficiency of Er³⁺ in LaF₃ nanocrystals is estimated to be 100% with a spectral bandwidth of 73 nm and a stimulated emission cross section of 3.3 × 10⁻²¹ cm², almost identical to the values of 61 nm (fwhm) and 4.1 × 10⁻²¹ cm² for 2.

Conclusion

Lanthanide clusters with internally coordinated Ln ions are synthetically possible, provided that a balance is struck between solvent and chalcogenido basicity. Key to this approach is the use of less basic chalcogens to chemically “cap” more basic LnE cores. These chalcogen rich materials have absorption and emission properties comparable to those of Er-doped solid-state materials and, as soluble compounds, are potentially useful for delivering emissive Er ions into organic polymers.

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Supporting Information Available: X-ray crystallographic files in CIF format for the crystal structures of 1 and 2. This material is available free of charge via the Internet at http://pubs.acs.org.

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Table 3. Comparison of the Fluorescence Lifetime and Phonon Frequencies of Some Reported Er-Containing Solid-State Materials

<table>
<thead>
<tr>
<th>Host</th>
<th>Lifetime (ms)</th>
<th>Phonon Frequency (cm⁻¹)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>sulfide</td>
<td>3.0</td>
<td>450–700</td>
<td>28</td>
</tr>
<tr>
<td>selenide</td>
<td>2.3</td>
<td>450–700</td>
<td>27</td>
</tr>
<tr>
<td>telluride</td>
<td>4</td>
<td>450–700</td>
<td>26</td>
</tr>
<tr>
<td>germanate</td>
<td>6</td>
<td>900</td>
<td>26</td>
</tr>
<tr>
<td>ZBLA fluoride glass</td>
<td>10</td>
<td>500</td>
<td>26</td>
</tr>
<tr>
<td>fluorides, chlorides</td>
<td>10–30</td>
<td>200–400</td>
<td>26</td>
</tr>
<tr>
<td>yttrium aluminum garnet</td>
<td>8</td>
<td>400</td>
<td>26</td>
</tr>
</tbody>
</table>

(49) Beck, G.; Nowacki, W. Naturwissenschaften 1938, 26, 495–6.