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Lanthanide Clusters with Internal Ln: Fragmentation and the Formation of Dimers with Bridging Se^{2-} and Se_2^{2-} Ligands

Louise Huebner, Anna Kornienko, Thomas J. Emge, and John G. Brennan*

Department of Chemistry and Chemical Biology, Rutgers, The State University of New Jersey,
610 Taylor Road, Piscataway, New Jersey 08854-8087

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Reactions of "$LnI_x(SePh)_{3-x}$" (Ln = Dy, Ho) with elemental S/Se give $(THF)_{14}Ln_{10}S_6(Se_2)_6I_6$. The compounds are composed of a Ln_6S_6 double cubane core, with two twisted "$Ln_2(SeSe)_3$" units condensed onto opposing rectangular sides of the Ln_6S_6 fragment. This deposition of Ln_2Se_6 totally encapsulates the two central Ln's with chalcogen atoms (four S and four Se atoms), excluding neutral THF donors or iodides from the two primary coordination spheres. Reactions of Ln_{10} clusters with a stronger Lewis base result in fragmentation and, in the case of Ln = Er, the isolation of $(py)_6Er_2(Se_2)(S_{0.8}Se_{0.2})I_2$, with two Ln(III) ions spanned by E^{2-} and $(EE)^{2-}$ ligands. The related homochalcogen dimers $(py)_6Ln_2(Se_2)(Se)Br_2$ (Ln = Ho, Yb) were prepared to establish that such molecules could be prepared rationally, and to confirm the isolability of E^{2-} ligands coordinated to only two sterically unconstrained Ln ions.

Introduction

With cluster chemistry representing the link between molecular and solid-state chemistry, considerable effort has been devoted to exploring synthetic methodologies that can produce monodisperse cluster compounds and to understanding the evolution of physical properties as a function of cluster size. Notable in this field are efforts focused on the group 12 metal chalcogenides (ME: M = Zn, Cd, Hg; E = S, Se, Te),[1−7] with equally stimulating descriptions of transition-metal cluster compounds[8−12] illustrating how structure and electronic properties are related to cluster size. While the chemistry of these covalent metal compounds continues to inspire, related work with the f elements has been less dramatic. Chalcogenido cluster chemistry of the lanthanides (Ln's) continues to evolve, but the oxygen, water, heat, and occasional light sensitivity of these materials has hindered progress in the area. Nevertheless, there now exists a broad spectrum of smaller cluster compounds, containing 4, 5, 6, 7, 8, and 10 Ln(III) ions connected by either E^{2-} or EE^{2-} ligands.[13−25] Some of these compounds have exhibited

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* Author to whom correspondence should be addressed. E-mail: bren@ccbmail.rutgers.edu.

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unconventional[19] or unprecedented[25] physical properties. Chemical reactivity studies show that these cluster compounds behave as ionic species,[18] with Ln bonding preferentially to more electronegative ligands.

The most recent addition to the family of LnE cluster compounds is $(THF)_{14}Er_{10}S_6(Se_2)_6I_6$, the first lanthanide cluster with internal Ln ions.[25] This compound was prepared with a heterochalcogen approach that uses more basic S^{2-} ligands to nucleate a core that is capped with external (Se_2) ligands.[25] This molecule was significant both because it was the first Ln cluster to contain internal Ln's that resemble solid-state Ln materials, and because it is highly emissive. To establish whether it might be possible to prepare Er-doped Ln_{10} clusters with electronically isolated Er ions (i.e., $(THF)_{14}ErLn_9S_6(Se_2)_6I_6$), and to determine just how robust this cluster framework was, we set out to establish the range of Ln's that would adopt a Ln_{10} framework, and to explore initial reactivity studies. We describe here the two additional Ln's that readily form the Ln_{10} cluster structure, and we show that the decametallic formulation is susceptible to fragmentation with stronger solvents. This leads to a description of the first lanthanide compounds with doubly bridging E^{2-} ligands that are not stabilized by sterically demanding ancillary ligands.

Experimental Section

General Methods. All syntheses were carried out under ultrapure nitrogen (Airtech), using conventional drybox or Schlenk techniques. Solvents (Fisher) were refluxed continuously over molten alkali metals or K/benzophenone or purified in a double column solvent purification system (Solvtech) and were collected immediately prior to use. Anhydrous pyridine (Aldrich) was purchased and refluxed over KOH. Ln's were purchased from Strem. Iodine, PhSeBr, and PhSeSePh were purchased from Aldrich and recrystallized from hexane. Melting points were taken in sealed capillaries and are uncorrected. IR spectra were taken on a Mattus Cygnus 100 FTIR spectrometer, and recorded from 4000 to 600 cm^{-1} as a Nujol mull on NaCl plates. Electronic spectra were recorded on a Varian DMS 100S spectrometer with the samples in a 0.10 mm quartz cell attached to a Teflon stopcock. Elemental analyses were performed by Quantitative Technologies, Inc. (Whitehouse, NJ).

Synthesis of $(THF)_{14}Dy_{10}S_6(Se_2)_6I_6 \cdot 3THF$ (1). Dy (0.75 g, 4.6 mmol), PhSeSePh (0.62 g, 2.0 mmol), iodine (1.27 g, 5.0 mmol), and Hg (0.05 g, 0.25 mmol) were combined in THF (60 mL). The mixture was stirred until all the metal was consumed to give a yellow solution. Elemental Se (0.16 g, 2.0 mmol) was added, the reaction mixture was stirred for 3 h, and then elemental S (0.032 g, 1.0 mmol) was added. After a day the orange solution was concentrated to ca. 40 mL, filtered, and layered with hexanes (12 mL). In 12 days yellow needle-shaped crystals (0.36 g, 36%) appeared which do not melt but turn dark brown at 253 °C. Anal. Calcd for $C_{68}H_{136}O_{17}I_6S_6Se_{12}Dy_{10}$: C, 17.2; H, 2.88. Found: C, 17.2; H, 2.92. The compound is insoluble in THF and does not show an optical absorption maximum from 300 to 800 nm in pyridine. IR: 3169 (s), 2923 (w), 2728 (s), 2679 (s), 1647 (s), 1576 (s), 1462 (w), 1377 (w), 1342 (s), 1304 (s), 1261 (s), 1155 (s), 1074 (w), 1020 (m), 913 (m), 861 (m), 801 (m), 722 (m) cm^{-1}.

Synthesis of $(THF)_{14}Ho_{10}S_6(Se_2)_6I_6 \cdot 3THF$ (2). Ho (0.33 g, 2.0 mmol), PhSeSePh (0.31 g, 1.0 mmol), iodine (0.15 g, 0.60 mmol), and Hg (0.05 g, 0.25 mmol) were combined in THF (60 mL). The mixture was stirred for 24 h. Elemental Se (0.19 g, 2.4 mmol) was added, and after 2 h elemental S (0.036 g, 1.2 mmol) was added to the yellow solution. In 3 days the solution was concentrated to 50 mL, filtered, and layered with hexanes (15 mL) to give yellow crystals (0.306 g, 32%) that do not melt but turn dark brown at 237 °C. Anal. Calcd for $C_{68}H_{136}O_{17}I_6S_6Se_{12}Ho_{10}$: C, 17.1; H, 2.88. Found: C, 17.2; H, 2.82. The compound is insoluble in THF and does not show an optical absorption maximum from 300 to 800 nm in pyridine. IR: 3168 (s), 2929 (w), 2728 (s), 2362 (s), 1845 (s), 1641 (s), 1460 (w), 1377 (w), 1343 (s), 1298 (s), 1261 (m), 1169 (s), 1075 (m), 1034 (s), 1011 (m), 956 (s), 913 (m), 849 (m), 802 (m), 723 (m), 668 (s) cm^{-1}. Monoclinic space group $C2/c$, with $a = 27.681(3)$ Å, $b = 18.119(2)$ Å, $c = 23.832(2)$ Å, $\alpha = 90°$, $\beta = 106.050(2)°$, $\gamma = 90°$, $V = 11488(2)$ Å^3, and $Z = 4$. A structure based on relatively low quality data is given in the Supporting Information.

Synthesis of $(py)_6Er_2I_2(Se_{0.2}S_{0.8})(SeSe) \cdot {}^1/_2py$ (3). Deep yellow crystals of $(THF)_{14}Er_{10}S_6(Se_2)_6I_6$[25] (0.48 g, 0.10 mmol) were dissolved in pyridine (30 mL), and after a day the orange solution was filtered (to remove an orange precipitate) and layered with hexanes (15 mL) to give orange crystals (0.23 g, 58% based on I) that turn brown at 274 °C but do not appear to melt up to 300 °C. Anal. Calcd for $C_{32.5}H_{32.5}N_{6.5}I_2S_{0.8}Se_{2.2}Er_2$: C, 31.3; H, 2.63; N, 7.31. Found: C, 31.4; H, 2.75; N, 6.74. UV−vis (4-ethylpyridine): 585 ($\epsilon = 57$), 551 ($\epsilon = 54$) nm. IR: 3077 (s), 2953 (w), 2924 (w), 2854 (m), 2600 (s), 2361 (s), 1980 (s), 1862 (s), 1630 (s), 1597 (m), 1580 (m), 1481 (m), 1459 (m), 1438 (w), 1376 (m), 1261 (m), 1216 (s), 1145 (s), 1089 (m), 1036 (m), 990 (s), 746 (m), 703 (w) cm^{-1}.

Synthesis of $(py)_6Ho_2Br_2(Se_2)Se \cdot {}^1/_2py$ (4). Ho (0.33 g, 2.0 mmol), PhSeBr (0.472 g, 2.0 mmol), and PhSeSePh (0.31 g, 1.0 mmol) were combined in pyridine (30 mL). The mixture was stirred until the metal was consumed (1 day) to give a transparent peach orange solution. Se (0.24 g, 3.0 mmol) was added to the mixture and the resulting mixture shaken until all of the Se was consumed (~2 min). The cherry red solution was filtered (25 mL), leaving some brown precipitate, and layered with hexanes (20 mL) to give peach yellow lathes (0.29 g, 23%) that turn black and melt at 170 °C. Anal. Calcd for $C_{32.5}H_{32.5}N_{6.5}Ho_2Se_3Br_2$: C, 31.5; H, 2.64; N, 7.34. Found: C, 31.4; H, 2.63; N, 7.33. The compound is insoluble in both THF and pyridine, and has an absorption at 430 nm in 4-ethylpyridine. IR: 3077 (s), 3028 (s), 2931 (s), 1632 (m), 1579 (s), 1464 (s), 1438 (s), 1377 (m), 1303 (w), 1261 (w), 1218 (m), 1144 (m), 1096 (w), 1068 (m), 1030 (w), 1007 (w), 988 (w), 874 (m), 803 (m), 744 (s), 701 (s), 621 (m), 600 (m) cm^{-1}.

Synthesis of $(py)_6Yb_2Br_2(Se_2)Se \cdot {}^1/_2py$ (5). Yb (0.346 g, 2.0 mmol), PhSeBr (0.47 g, 2.0 mmol), and PhSeSePh (0.31 g, 1.0 mmol) were combined in pyridine (25 mL). The mixture was stirred until the metal was consumed (1 day) to give a transparent dark purple solution. Se (0.24 g, 3.0 mmol) was added to the mixture and the resulting mixture shaken until all of the Se was consumed (~2 min). The dark brown solution was filtered (20 mL), leaving a trace black precipitate, and layered with hexanes (10 mL) to give dark red needles (0.35 g, 28%) that turn black and melt at 255 °C. Anal. Calcd for $C_{32.5}H_{32.5}N_{6.5}Yb_2Se_3Br_2$: C, 31.1; H, 2.61; N, 7.25. Found: C, 31.1; H, 2.77; N, 6.86. The compound is insoluble in

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Table 1. Summary of Crystallographic Details for **1** and **3**−**5**[a]

	1	**3**	**4**	**5**
empirical formula	$C_{68}H_{136}Dy_{10}I_6O_{17}S_6Se_{12}$	$C_{32.5}H_{32.5}Er_2I_2N_{6.5}S_{0.82}Se_{2.18}$	$C_{32.5}H_{32.5}Br_2Ho_2N_{6.5}Se_3$	$C_{32.5}H_{32.5}Br_2Yb_2N_{6.5}Se_3$
fw	4752.05	1300.66	1240.71	1256.93
space group	*C*2/*c*	*C*2/*c*	*C*2/*c*	*C*2/*c*
a (Å)	27.7606(8)	48.053(4)	48.065(3)	47.710(4)
b (Å)	18.1961(5)	9.6756(7)	9.6714(6)	9.6254(8)
c (Å)	23.9329(7)	16.9322(13)	16.559(1)	16.4448(14)
β (deg)	106.042(1)	93.821(2)	94.376(1)	94.234(2)
V (Å^3)	11618.6(6)	7855(1)	7675(1)	7531(1)
Z	4	8	8	8
D_{calcd} (g/cm^{-3})	2.717	2.200	2.147	2.217
temp (K)	100(2)	100(2)	100(2)	100(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073
abs coeff (mm^{-1})	11.904	7.907	9.053	9.990
$R(F)^b$ $[I > 2\sigma(I)]$	0.0509	0.0589	0.0482	0.0373
$R_w(F^2)^c$ $[I > 2\sigma(I)]$	0.1129	0.1268	0.0958	0.0678

[a] Additional crystallographic details are given in the Supporting Information. [b] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $R_w(F^2) = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

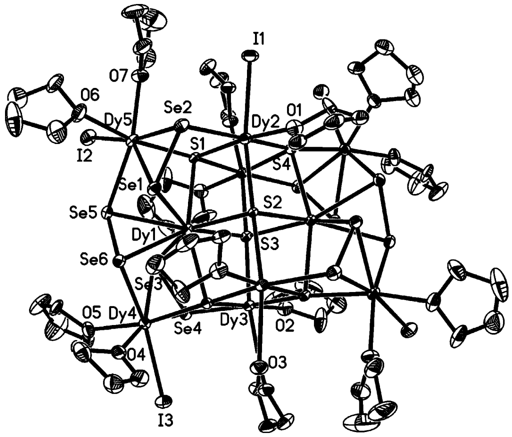

Figure 1. Molecular structure of the decanuclear heterochalcogen clusters **1** and **2** with the thermal ellipsoids drawn at the 50% probability level for **1**.

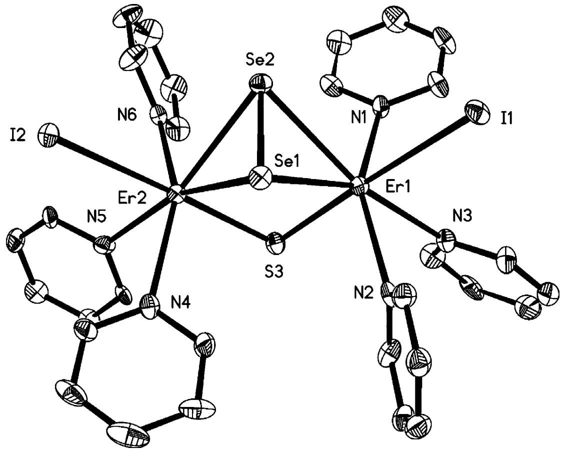

Figure 2. Molecular structure of the common structure for **3**−**5**, with thermal ellipsoids drawn at the 50% probability level for **3**.

both THF and pyridine and does not show an optical absorption maximum from 300 to 800 nm in 4-ethylpyridine. IR: 3077 (s), 3024 (s), 2925 (s), 1632 (m), 1597 (s), 1580 (s), 1438 (s), 1377 (m), 1302 (w), 1261 (m), 1216 (m), 1146 (m), 1095 (w), 1068 (m), 1030 (w), 1007 (w), 991 (w), 952 (w), 877 (m), 806 (m), 746 (s), 702 (s), 623 (m), 602 (m) cm^{-1}.

X-ray Structure Determination of 1 and 3−5. Data for **1** and **3**−**5** were collected on a Bruker Smart APEX CCD diffractometer with graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) at 100 K. The data were corrected for Lorenz effects, polarization, and absorption, the latter by a multiscan (SADABS)[26] method. The structures were solved by Patterson or direct methods (SHELXS86).[27] All non-hydrogen atoms were refined (SHELXL97)[28] on the basis of F_{obs}^2. All hydrogen atom coordinates were calculated with idealized geometries (SHELXL97). Scattering factors (f_o, f', f'') are as described in SHELXL97. Crystallographic data and final *R* indices for **1** and **3**−**5** are given in Table 1. An ORTEP diagram[28] for isostructural **1** and **2** is shown in Figure 1, while an ORTEP diagram for isostructural **3**−**5** is shown in Figure 2. Significant bond geometries for **1** are given in Table 2, and significant bond geometries for **3**−**5** are given in Table 3. Complete crystallographic details for **1**−**5** are given in the Supporting Information.

Results

The decametallic formulation $(THF)_{14}Ln_{10}S_6(Se_2)_6I_6$ originally found for Er[25] can also be isolated for Dy (**1**) and Ho (**2**), but does not appear to form for the earlier or latter lanthanides. Both compounds are isostructural with the Er derivative, containing a distorted double cubane arrangement of Ln_6S_6, and capped to either side with two Ln_2Se_3 units such that the internal Ln of the cubane is now totally encapsulated with chalcogen donors (four S and four Se atoms). An ORTEP diagram for the common structure of **1** and **2** is given in Figure 1, with significant bond lengths for **1** given in Table 2.

These larger clusters fragment upon exposure to a stronger Lewis base. When $(THF)_{14}Er_{10}S_6(Se_2)_6I_6$ is dissolved in pyridine and the resultant solution is saturated, crystals of $(py)_6Er_2(Se_{0.2}S_{0.8})(Se_2)I_2$ (**3**) are isolated and characterized by low-temperature X-ray diffraction (reaction 1). Figure 2

$$(THF)_{14}Er_{10}S_6(Se_2)_6I_6 + py \rightarrow (py)_6Er_2(Se_{0.2}S_{0.8})(Se_2)I_2 \quad (1)$$

shows an ORTEP diagram of **3**, with significant distances and angles for **3** given in Table 3. Product **3** is a dimer, with the two Er atoms bridged by an η^2-η^2-Se_2^{2-} and a single

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(26) Bruker-ASX. *SADABS, Bruker Nonius area detector scaling and absorption correction*, version 2.05; Bruker-AXS Inc.: Madison, WI, 2003.

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Table 2. Significant Distances (Å) for 1[a]

Dy(1)−S(1)	2.817(2)	Dy(1)−Se(6)	2.9109(11)	Dy(2)−I(1)	3.0296(8)
Dy(1)−S(4)′	2.846(2)	Dy(1)−Se(3)	2.9661(11)	Dy(4)−I(3)	3.0595(9)
Dy(1)−S(2)	2.859(2)	Dy(1)−Se(1)	3.0503(11)	Dy(5)−I(2)	3.0750(9)
Dy(1)−S(3)	2.881(2)	Dy(1)−Se(5)	3.0625(11)	Dy(2)−O(1)	2.340(7)
Dy(2)−S(4)	2.686(2)	Dy(2)−Se(2)	2.8510(11)	Dy(3)−O(2)	2.321(7)
Dy(2)−S(2)	2.7122(5)	Dy(3)−Se(4)	2.8693(11)	Dy(3)−O(3)	2.334(7)
Dy(2)−S(1)	2.736(2)	Dy(4)−Se(3)	2.8047(11)	Dy(4)−O(5)	2.362(7)
Dy(3)−S(3)	2.6274(6)	Dy(4)−Se(4)	2.9011(12)	Dy(4)−O(4)	2.390(7)
Dy(3)−S(4)′	2.691(2)	Dy(4)−Se(6)	2.9986(12)	Dy(5)−O(6)	2.343(8)
Dy(3)−S(1)′	2.694(2)	Dy(5)−Se(1)	2.7868(11)	Dy(5)−O(7)	2.393(7)
Dy(4)−S(4)′	2.711(2)	Dy(5)−Se(2)	2.9228(12)	Se(1)−Se(2)	2.3985(15)
Dy(5)−S(1)	2.700(2)	Dy(5)−Se(5)	2.9269(12)	Se(3)−Se(4)	2.4093(15)
				Se(5)−Se(6)	2.3789(15)

[a] Symmetry transformations used to generate equivalent (primed) atoms: $-x + 1, y, -z + 1/2$.

Table 3. Significant Distances (Å) and Angles (deg) for **3**−**5**

3		4		5	
Er(1)−S(3)	2.612(2)	Ho(1)−Se(1)	2.7344(9)	Yb(1)−Se(1)	2.7086(9)
Er(2)−S(3)	2.630(2)	Ho(2)−Se(1)	2.7237(8)	Yb(2)−Se(1)	2.6858(9)
Er(1)−Se(2)	2.8812(12)	Ho(1)−Se(2)	2.9074(9)	Yb(1)−Se(2)	2.8736(9)
Er(2)−Se(2)	2.8922(13)	Ho(2)−Se(2)	2.8879(9)	Yb(2)−Se(2)	2.8621(9)
Er(1)−Se(1)	2.8505(12)	Ho(1)−Se(3)	2.9034(9)	Yb(1)−Se(3)	2.8652(9)
Er(2)−Se(1)	2.8886(13)	Ho(2)−Se(3)	2.8731(9)	Yb(2)−Se(3)	2.8462(9)
Er(1)−I(1)	3.0582(9)	Ho(1)−Br(1)	2.8411(9)	Yb(1)−Br(1)	2.8016(9)
Er(2)−I(2)	3.0874(9)	Ho(2)−Br(2)	2.8151(9)	Yb(2)−Br(2)	2.7744(9)
Er(1)···Er(2)	3.6926(8)	Ho(1)···Ho(2)	3.7190(7)	Yb(1)···Yb(2)	3.7391(6)
Er(1)−N(3)	2.504(9)	Ho(1)−N(1)	2.486(7)	Yb(1)−N(1)	2.457(7)
Er(1)−N(2)	2.527(9)	Ho(1)−N(2)	2.502(7)	Yb(1)−N(2)	2.445(6)
Er(1)−N(1)	2.532(9)	Ho(1)−N(3)	2.507(6)	Yb(1)−N(3)	2.457(7)
Er(2)−N(6)	2.488(9)	Ho(2)−N(4)	2.518(6)	Yb(2)−N(4)	2.468(6)
Er(2)−N(5)	2.502(9)	Ho(2)−N(5)	2.542(7)	Yb(2)−N(5)	2.509(7)
Er(2)−N(4)	2.509(9)	Ho(2)−N(6)	2.541(7)	Yb(2)−N(6)	2.477(7)
Se(1)−Se(2)	2.3567(16)	Se(2)−Se(3)	2.3630(11)	Se(2)−Se(3)	2.3591(12)
Er(1)−S(3)−Er(2)	89.55(7)	Ho(2)−Se(1)−Ho(1)	87.98(2)	Yb(2)−Se(1)−Yb(1)	87.76(3)
Er(1)−Se(2)−Er(2)	79.52(3)	Ho(2)−Se(2)−Ho(1)	81.71(2)	Yb(2)−Se(2)−Yb(1)	81.37(2)
Er(1)−Se(1)−Er(2)	80.09(3)	Ho(2)−Se(3)−Ho(1)	82.03(2)	Yb(2)−Se(3)−Yb(1)	81.79(2)

μ_2-E^{2-} that is compositionally disordered (80% S, 20% Se). There is a terminal I^- on each Er and three pyridine ligands completing the distorted pentagonal bipyramidal coordination sphere.

Attempts to rationally synthesize analogues of dimer **3** using stoichiometric Ln/I and either mixtures of S/Se or Se led to product mixtures contaminated with $[(py)_5LnI_2][I]$ and/or $[(py)_5LnI_2][I_3]$.[30] However, by replacing I with Br, dimeric $(py)_6Ln_2Se(Se_2)Br_2$ (Ln = Ho, Yb) could be isolated as pure materials in high yield. Complete low-temperature X-ray diffraction analyses of **4** and **5** were obtained, and significant bond lengths and angles for **4** and **5** are given in Table 3. Both **4** and **5** are isostructural with **3**, containing terminal bromide ligands and doubly bridging Se^{2-} and Se_2^{2-} ligands. The Ho compound exhibits the deep yellow color associated with the Se_2^{2-} ligand (λ_{max} = 440 nm),[31−33] while the Yb compound is dark red because of relatively low energy Se to Yb charge-transfer absorptions.[34] In the structures, the Ln−E^{2-}−Ln angles are 89.55(7)° (**3**), 87.98(2)° (**4**), and 87.76(3)° (**5**).

Discussion

Along with the Er derivative, compounds **1** and **2** represent the only examples of lanthanide clusters with "internal" Ln ions. This "heterochalcogen" approach, by which more nucleophilic chalcogens are buried with the cluster core and less nucleophilic chalcogens "cap" the cluster surface, is a potentially general approach to the synthesis of both larger clusters and ternary solid-state materials. This ability to prepare clusters with both internal and surface Ln is key to the eventual goal of evaluating how physical properties evolve with cluster size. Unfortunately, the series of Ln_{10} compounds spans only three Ln's in the series, presumably because the effect of changing metal radii on structure is magnified by the presence of ten metals. While the other Ln's may in fact form Ln_{10} structures in solution, only three pack effectively enough in a lattice to form crystalline products. In addition, the fact that the Ln_{10} structure contains six-, seven-, and eight-coordinate Ln's must also limit the number of Ln's that can adopt this structure, as only on the right-hand side of the series do Ln's typically adopt six-coordinate geometries.

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Fragmentation of the Er_{10} cluster with a strong Lewis base to give **3** is significant in three ways.

First, this was the first example of a nonorganometallic Ln compound to contain two-coordinate E^{2-} ligands. Previous examples of Ln−E−Ln linkages were obtained only with ancillary Cp* ligands that were, at the time,[35,36] specifically introduced to inhibit any ligand redistribution processes that would yield higher coordinate E^{2-}; i.e., $Cp^*_2Ln{-}E{-}Ln{-}Cp^*_2$ does not disproportionate to give Cp^*_3Ln and $[Cp^*LnE]_x$. In the present inorganic systems, doubly bridging linkages were always assumed to be a possible intermediate in the process by which $Ln(EPh)_3$ reduces E to give PhEEPh and E^{2-}, and the reproducible isolation of **4** and **5** indicates that such compounds are more accessible than previously thought.

Second, dimer **3** has a compositionally disordered E^{2-} (S^{2-}/Se^{2-}) site, isolated from a source that contained only S^{2-} and $(SeSe)^{2-}$ ligands. The disorder in **3** clearly indicates that EE^{2-} ligands are reactive, and processes such as the disproportionation of EE^{2-} (reaction 2) are potentially

$$2(EE)^{2-} \leftrightarrow E^{2-} + (EEE)^{2-} \qquad (2)$$

interesting areas of reactivity because the $(EEE)^{2-}$ product is both a potential four-electron oxidant and a natural unit for linking extended arrays of Ln's.[37] An alternative explanation for the observation of Se^{2-}, namely, the reaction of Se_2^{2-} with S^{2-} to give $(SeS)^{2-}$, is presumably less favorable because the greater electronegativity of S relative to Se would seem to favor a fully reduced sulfur, but clearly this alternative reactivity cannot be ruled out with the available data. Such disorder has been seen previously in mixed S/Se compounds.[38−40]

Finally, fragmentation of a Ln_{10} cluster to give dimer **3** illustrates an important principle in Ln cluster synthesis; in the elusive search for larger particles, solvent choice is crucial. More basic solvents favor the formation of smaller particles with more Ln−solvent interactions, while less basic solvents can be used to enhance the tendency of these systems to form large cluster compounds. This contrasts dramatically with the cluster chemistry of the transition elements, where the steric properties of the neutral donors, rather than donor strength, were the important properties that governed cluster isolation.[6] Given this cluster fragmentation, the ability to work in hydrocarbon solvents[41−43] becomes an increasingly important capability in the search for large particles.

The Ln−E−Ln angles in **3** and **4** are distinctly nonlinear. In the previously mentioned LnCp* compounds and similar actinide molecules the M−E−M angles were considerably distorted from the ideal right angle geometries adopted by so many ER_2 compounds, with, for example, an Yb−Se−Yb angle[36] of 171° in $Cp^*_2Yb{-}Se{-}YbCp^*_2$ or the U−S−U angle[44] of 164.9(5)° in $Cp_3U{-}S{-}UCp_3$. It was never clear, in these organometallic molecules, whether some form of E-to-M π donation was responsible for this geometry or if simple Cp*−Cp* repulsive interactions effectively opened the M−E−M angle. Along these lines, there are a number of related oxo linkages that are distinctly linear.[45−48] Certainly in the present system, the Ln−E−Ln angles are nearly 90°, and any E-to-Ln π donation that may be present is not significant enough to result in a linear arrangement at the central E^{2-}, as might be found in a network lattice rather than the present molecular geometry.

That these compounds can be isolated is likely a reflection of their extreme insolubility, rather than a reflection of stability associated with the two-coordinate E^{2-}. In pyridine, the chalcogen-rich compound $(py)_8Yb_4Se_9I_2$ can be prepared and redissolved, but increasing the ratio of I to Ln eventually leads to the isolation of $[(py)_5YbI_2][I]$ and eventually $[(py)_5YbI_2][I_3]$. Switching from I to Br decreases the tendency to have neutral donors cleave the Ln−X bond and thus avoids the initial formation of ionic products. Once isolated, these dimers are totally insoluble in either THF or pyridine, and dissolve only in 4-Et(py).

Conclusions

The decameric formulation $(THF)_{14}Ln_{10}S_6(SeSe)_6I_6$ can be isolated for Ln = Dy, Ho, and Er. Exposure of these compounds to a more basic solvent results in cluster fragmentation to give dimeric compounds with two-coordinate E^{2-} and EE^{2-} ligands. Rational approaches to these dimeric molecules are successful only when iodide is replaced by bromide, due to the propensity of iodide to form chalcogen-free salts when there is any appreciable concentration of I^- present in the reaction mixture.

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Supporting Information Available: X-ray crystallographic files in CIF format for the crystal structures of **1**−**5**. This information is available free of charge via the Internet at http://pubs.acs.org.

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