Chalcogen-Rich Lanthanide Clusters: Cluster Reactivity and the Influence of Ancillary Ligands on Structure

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Abstract: Ytterbium metal reacts with PhEEPh (E = S, Se, Te) and elemental Se in pyridine to give $(pyridine)_8Yb_4(SeSe)_2(Se)_2(\mu_2\text{-}SPh)_2(SPh)_2$, $(py)_8Yb_4Se(SeSe)_3(SeSeSePh)(Se_{0.38}SePh)$, and $(py)_8Yb_4Se(SeSe)_3(SeSeTePh)(SeTePh)$, respectively. The SePh and TePh compounds contain a square array of Ln(III) ions all connected to a central Se^{2-} ligand. Three edges of the square are bridged by diselenide ligands, with the fourth SeSe unit coordinating to an EPh ligand that has been displaced from an inner Yb coordination sphere. Differences in the two compounds have their origin in the relative strength of the Yb−E(Ph) bond. In the TePh compound, there is a complete insertion of Se into the remaining Yb−Te(Ph) bond to give a terminal SeTePh ligand, while in the SePh compound there is a compositional disorder in the structure comprised of a terminal SePh ligand and a minor component that has Se inserted into the Yb−Se(Ph) bond to give a terminal SeSePh ligand. The thiolate compound differs dramatically, crystallizing as a rhombohedral array of four Yb(III) ions connected by a pair of $\mu_3\text{-}Se^{2-}$ ligands, with the edges of the rhombus spanned by alternating diselenide and SPh. The SPh coordinate directly to Yb(III) ions in terminal or bridging modes. Cluster interconversion is facile: $(py)_4Yb(SePh)_2$ reduces $(py)_8Yb_4Se(SeSe)_3(SeSeSePh)(Se_{0.38}SePh)$ to give the cubane cluster $[(py)_2YbSe(SePh)]_4$, and the cubane reacts with elemental Se to give $(py)_8Yb_4Se(SeSe)_3(SeSeSePh)(Se_{0.38}SePh)$. Upon thermolysis, these compounds give $YbSe_x$.

Introduction

Interest in lanthanide (Ln; Ln = La−Lu) compounds with only chalcogen (E; E = S, Se, or Te) based anionic ligands continues to be motivated both by a fundamental interest in the nature of the Ln−E bond, and by the potential applications of Ln ions in chalcogenido based pigments[1] and optical fibers.[2] Only in the past decade, with the synthesis of $Ln(ER)_x$ (R = organic; $x = 2, 3$) compounds, has it become apparent that highly electronegative, sterically saturating ancillary ligands (e.g. Cp*) are not a prerequisite for the successful isolation and characterization of molecular compounds with Ln−E bonds.[3] Synthetic investigations into the stability, structure, and physical properties of $Ln(ER)_x$ compounds have been fruitful, with the Ln chemistry of the benzenechalcogenolate (EC_6H_5, or EPh) ligand[4] developing most fully. Sterically demanding R groups have also been employed extensively,[5] and electronegative R groups (e.g. C_6F_5 or $2\text{-}NC_5H_4$)[6] have also be used to deliver Ln compounds with pre-ordained structural or physical properties.

Chalcogenido (E^{2-}) cluster compounds of the lanthanides were subsequently investigated. The most general synthetic approach to these materials involves the reduction of elemental E by $Ln(EPh)_3$, with concomitant oxidative elimination of PhEEPh.[7] This reactivity has been controlled to give crystalline homo- and heterometallic clusters, heterovalent compounds, and clusters with most combinations of Ln, E, EPh, and neutral donor ligands in high yields. The cubic octanuclear array of Ln ions in the $Ln_8E_6(EPh)_{12}$ series is observed for most Ln (Ce through Er),[7a−d] while the smaller Ln (Tm and Yb) tend to form clusters with cubane[7e] based geometries. Because the fundamental structural, electronic, and magnetic properties of the molecular chalcogenolate compounds were well understood, the corresponding properties of these cluster compounds were readily interpreted. In these cluster compounds, spin systems are isolated, charge transfer absorptions dominate the electronic spectra of redox active Sm, Eu, and Yb compounds, and with few exceptions, the chemistry can be described as entirely ionic.

Most recently, a high-yield synthesis of chalcogen-rich Ln clusters with disulfide ligands has been reported.[8] The initial isolation of $(THF)_6Yb_4S(SS)_4I_2$ led to the suggestion that

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compounds with EE ligands may be more stable than compounds with E^{2-} ligands. As yet, however, there is no evidence to indicate the facility with which compounds containing EE^{2-} or E^{2-} ligands can be interconverted.

The synthetic investigations reported here, which describe the first high-yield syntheses of Ln clusters with (SeSe) ligands, reveal a rich structural chemistry in which ancillary EPh (E = S, Se, Te) ligands play a significant role in determining the crystal and molecular structure of the isolated product. Cluster interconversion is probed, the Ln−E−E′−R connectivity is first noted in Ln chemistry, and the utility of these chalcogen-rich compounds for the preparation of chalcogenido clusters or solid-state $LnSe_x$ materials is demonstrated.

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 collected immediately prior to use. Anhydrous pyridine (Aldrich) was purchased and refluxed over KOH. PhSeSePh and PhSSPh were purchased from Alrdich and recrystallized from hexane. PhTeTePh was prepared according to literature procedures.[9] Yb, Hg, S, Se, and Te were purchased from Strem. There appears to be no difference in reactivity when either commercial Se/Te or freshly sublimed Se/Te are used. 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). These compounds are sensitive to the thermal dissociation of neutral donor ligands at room temperature and lose lattice solvents within minutes. Calculated analytical values for the lattice desolvated materials are given in parentheses. Experimentally determined analyses for samples isolated from mother liquors more than 30 min are given in parentheses. NMR spectra were obtained on either Varian Gemini 200 MHz or Varian 300 or 400 MHz NMR spectrometers and chemical shifts are reported in δ (ppm).

Synthesis of $(py)_8Yb_4(\mu_4\text{-}Se)(\mu_2\text{-}SeSe)_3(\mu_2\text{-}SeSeSePh)(Se_{0.38}SePh)\cdot 2py$ (1): Yb (346 mg, 2.0 mmol), diphenyl diselenide (312 mg, 1.0 mmol), and Hg (50 mg, 0.25 mmol) were stirred in pyridine (30 mL) for 24 h to give a deep violet solution with unreacted metal. Elemental Se (355 mg, 4.5 mmol) was added, and after 7 h the black/brown solution was filtered into a tube with a diameter of 41 mm, concentrated to 20 mL, and layered with hexanes (3 mL) to give dark red crystals (0.892 g, 70%) that appear to desolvate at 125 °C and decompose at 176 °C. Anal. Calcd for $C_{62}H_{60}N_{10}Se_{11.38}Yb_4$: C, 29.4 (26.6); H, 2.38 (2.15); N, 5.55 (4.79). Found: C, 29.4 (26.7); H, 2.43 (2.13); N, 5.61 (4.97). UV−Vis (THF): 351 ($\epsilon = 4.2 \times 10^3$), 500 ($\epsilon = 1.1 \times 10^3$) nm. The visible spectrum is featureless in pyridine. IR: 3076 (s), 2728 (s), 2669 (s), 2400 (s), 2289 (s), 2019 (s), 1912 (s), 1860 (s), 1677 (s), 1631 (s), 1596 (s), 1579 (m), 1537 (s), 1460 (w), 1377 (w), 1289 (s), 1260 (w), 1216 (s), 1192 (s), 1143 (m), 1093 (w), 1068 (w), 1020 (w), 904 (s), 874 (s), 799 (s), 757 (s), 743 (m), 722 (s), 701 (w), 661 (s), 645 (s), 623(s) cm^{-1}. The ^1H NMR spectrum (C_5D_5N, 20 °C) contained resonances from rapidly exchanging free and coordinated pyridine (8.71, 7.56, 7.20 ppm).

Synthesis of $[(py)_2YbSe(SePh)]_4$ from 1: 1 (1.05 mg, 0.45 mmol) and $(py)_4Yb(SePh)_2$[4d] (1.97 mg, 2.2 mmol) were combined in pyridine (50 mL) and the temperature was raised to 40 °C for 30 min. After 1 day the deep red solution was filtered, concentrated to 25 mL, and layered with hexanes (10 mL) to give dark red crystals (0.46 mg, 46%) of $[(py)_2YbSe(SePh)]_4$ that were identified[7e] by mp, IR, and UV−vis spectroscopy, and low-temperature single-crystal unit cell determination.

Synthesis of 1 from $[(py)_2YbSe(SePh)]_4$: Crystalline $[(py)_2YbSe(SePh)]_4\cdot py$ (0.96 g, 0.39 mmol) and elemental Se (1.54 g, 1.9 mmol) were combined in pyridine (50 mL) at room temperature. After 1 day the solution was filtered, concentrated to 30 mL, and layered with hexanes (3 mL) to give black-red crystals (0.51 g, 51%) of **2** that were identified by mp, IR, UV−vis spectroscopy, and unit cell determination by low-temperature single-crystal X-ray diffraction.

Synthesis of $(py)_9Yb_4(\mu_4\text{-}Se)(\mu_2\text{-}SeSe)_2(\mu_2\text{-}SeSeTe(Ph)SeSe)(SeTePh)\cdot py$ (2): Yb (346 mg, 2.0 mmol), diphenyl ditelluride (409 mg, 1.0 mmol), and Hg (50 mg, 0.25 mmol) were stirred in pyridine (30 mL) for 24 h to give a deep violet solution with unreacted metal. Elemental Se (355 mg, 4.5 mmol) was added and after 7 h the black/brown solution was filtered into a tube with a diameter of 41 mm, concentrated to 20 mL, and layered with hexanes (2 mL) to give black-red crystals (0.773 g, 57%) that desolvate at 144 °C but do not melt up to 320 °C. Anal. Calcd for $C_{62}H_{60}N_{10}Se_{10}Te_2Yb_4$: C, 27.8 (24.7); H, 2.25 (2.00); N, 5.24 (4.46). Found: C, 27.7; H, 2.13; N, 4.97. UV−Vis (THF): 381 ($\epsilon = 2.7 \times 10^3$) nm. UV−Vis (pyr): 370 ($\epsilon = 8.8 \times 10^2$) nm. IR: 3076 (s), 2724 (s), 2670 (s), 2399 (s), 2289 (s), 1975 (s), 1912 (s), 1860 (s), 1677 (s), 1632 (s), 1596 (m), 1579 (m), 1536 (s), 1461 (w), 1439 (w), 1377 (w), 1306 (s), 1261 (s), 1216 (m), 1170 (s), 1144 (m), 1092 (s), 1067 (m), 1030 (m), 1005 (s), 990 (s), 947 (s), 875 (s), 799 (s), 757 (s), 743 (m), 731 (s), 701 (w), 623 (s) cm^{-1}. The ^1H NMR spectrum (NC_5D_5, 20 °C) contained resonances from displaced pyridine (8.71, 7.56, and 7.20 ppm).

Synthesis of $(py)_8Yb_4(\mu_3\text{-}Se)_2(\mu_2\text{-}SeSe)_2(\mu_2\text{-}SPh)_2(SPh)_2\cdot 2py$ (3): Yb (346 mg, 2.0 mmol), diphenyl disulfide (218 mg, 1.0 mmol), and Hg (50 mg, 0.25 mmol) were stirred in pyridine (30 mL) for 24 h to give a black-purple solution with unreacted metal. Elemental Se (355 mg, 4.5 mmol) was added, and after 2 days the deep red solution was filtered and concentrated to 25 mL to give red crystals (0.453 g, 35%) that do not melt but slowly turn dark orange, brown, and finally black by 320 °C. Anal. Calcd for $C_{74}H_{70}N_{10}S_4Se_6Yb_4$: C, 34.4 (31.7); H, 2.73 (2.50); N, 5.45 (4.64). Found: C, (31.6); H, (2.46); N, (4.61). UV−Vis (*tert*-butylpyridine): 380 ($\epsilon = 316$), 445 ($\epsilon = 136$) nm. IR: 3146 (s), 3077 (m), 2724 (s), 2670 (s), 2376 (s), 2290 (s), 2036(s), 1976 (s), 1912 (s), 1860 (s), 1774 (s), 1686 (s), 1656 (s), 1631 (s), 1596 (m), 1579 (w), 1538 (s), 1461 (w), 1377 (w), 1306 (s), 1261 (s), 1234 (s), 1216 (m), 1188 (s), 1170 (s), 1144 (m), 1127 (s), 1083 (s), 1068 (s), 1030 (m), 1003 (s), 991 (s), 939 (s), 889 (s), 799 (s), 744 (m), 731 (s), 701 (w), 654 (s), 621(s) cm^{-1}. The ^1H NMR spectrum (NC_5D_5, 20 °C) contained resonances from pyridine (8.71, 7.56, and 7.20 ppm). The compound is not soluble in either THF or toluene and is sparingly soluble in pyridine.

X-ray Structure Determination of 1−3. Data for **1**−**3** were collected on an Enraf-Nonius CAD4 diffractometer with graphite monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) at −120 °C. The check reflections measured every hour showed less than 3% intensity variation. The data were corrected for Lorenz effects and polarization,

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Table 1. Summary of Crystallographic Details for **1**, **2**, and **3**

compd	**1**	**2**	**3**
empirical formula	$C_{37}H_{35}N_5S_2Se_3Yb_2$	$C_{62}H_{60}N_{10}Se_{11.38}Yb_4$	$C_{62}H_{60}N_{10}Se_{10}Te_2Yb_4$
fw	2535.53	2682.16	1196.78
space group (no.)	$P2_1/c$ (14)	$P2_1/c$ (14)	$P\bar{1}$ (2)
a (Å)	12.405(6)	12.305(6)	10.928(9)
b (Å)	30.97(2)	31.220(19)	12.960(9)
c (Å)	18.881(10)	19.105(9)	14.658(3)
α (deg)	90.00	90.00	91.27(5)
β (deg)	92.25(4)	91.25(4)	89.89(5)
γ (deg)	90.00	90.00	110.14(6)
V (Å$^{3)}$	7249(7)	7338(7)	1949(2)
Z	4	4	2
D(calcd) (g/cm^{-3})	2.323	2.428	2.040
temperature (°C)	−120	−120	−120
λ (Å)	0.71073	0.71073	0.71073
abs coeff (mm^{-1})	10.869	10.835	7.712
$R(F)^a$ $[I > 2\ \sigma(I)]$	0.056	0.068	0.034
$R_w(F^2)^a$ $[I > 2\ \sigma(I)]$	0.141	0.161	0.080

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

as well as absorption, the latter by a numerical (SHELX76)[10] method. The structures were solved by Patterson or direct methods (SHELXS86).[11] All non-hydrogen atoms were refined (SHELXL97) based upon F_{obs}^2. All hydrogen atom coordinates were calculated with idealized geometries (SHELXL97).[12] Scattering factors (f_o, $f\,'$, $f\,''$) are as described in SHELXL97. Crystallographic data and final R indices for **1**−**3** are given in Table 1. Significant bond distances and angles for **1**−**3** are given in Tables 4, 2, and 3, respectively. Complete crystallographic details are given in the Supporting Information. ORTEP diagrams[13] for the core regions of **1**−**3** are shown in Figures 3, 1, and 2, respectively.

Results

Diselenido clusters of Yb are isolated in high yields from the reduction of PhEEPh/Se mixtures by elemental Yb in pyridine. Addition of PhEEPh should precede addition of elemental Se to avoid what appears to be passivation of the metal surface by elemental E in pyridine. While the general structure of the preferred product resembles the cluster core observed in related sulfur-rich Ln chemistry,[8] there are dramatic differences in the structures of all three products that can clearly be related to the identity of the chalcogenolate ligands present.

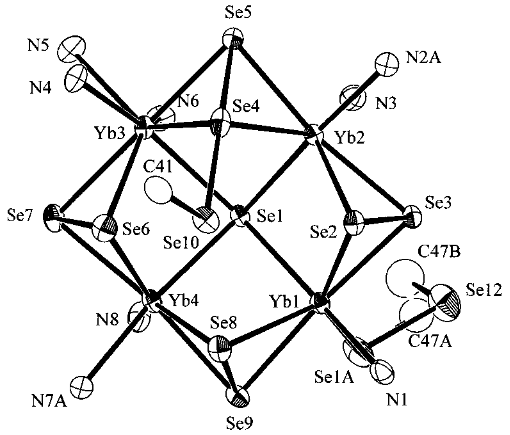
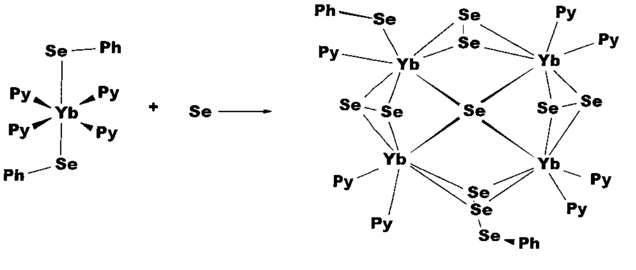


Figure 1. Core bonding region of the molecular structure of $(py)_8Yb_4Se(SeSe)_3(SeSeSePh)(Se_{0.38}SePh)$ (**1**) showing the major product with the terminal SePh ligand (Se1A bonds to C47A), and the minor cocrystallized product with Se inserted into the Yb−Se(Ph) bond to give the terminal Se−Se−Ph ligand (Se1A bonds to Se12), with the C and H atoms removed. Thermal ellipsoids are drawn at the 50% probability level.

Scheme 1



The all-selenium compound $(py)_8Yb_4Se(SeSe)_3(SeSeSePh)(Se_{0.38}SePh)$ (**1**) is prepared at room temperature by reducing PhSeSePh and Se metal with elemental Yb in pyridine (reaction 1, Scheme 1). The product was characterized by conventional techniques and by low-temperature single-crystal X-ray dif-

$$4Yb + PhSePh + xSe \rightarrow (py)_8Yb_4Se(SeSe)_3(SeSeSePh)(Se_{0.38}SePh)\ (x = 6\text{-}9) \quad (1)$$

fraction, from which the structure was shown to contain a square array of Yb(III) ions connected by a central Se^{2-} ligand, with three edges of the square bridged by μ_2-SeSe ligands (Figure 1; Se1A bonds to C47A). One of the two remaining SePh ligands has been displaced from the metal coordination sphere, and instead coordinates to the fourth diselenido unit to give a μ_2-η^2-η^2-$SeSeSePh^{3-}$ ligand. There is a clear interaction between PhSe(10) and one of the edge-spanning diselenides. The coordinated diselenido unit, Se(4)−Se(5), interacts strongly with the SePh, such that the Se(10)−Se(4) bond at 2.598(3) Å is actually 0.160 Å shorter than the Se(4)−Se(5) bond. This Se(4)−Se(5) distance of 2.758(3) Å is longer, by about 0.34 Å, than the Se−Se bonds in the remaining three Se_2 units in the structure. Of these three Se_2 units, the bond between Se(6) and Se(7) is also slightly longer, by ca. 0.06 Å, than the bonds in the remaining two clearly unperturbed diselenido ligands (see Table 2). Consistent with this observation, the bond length

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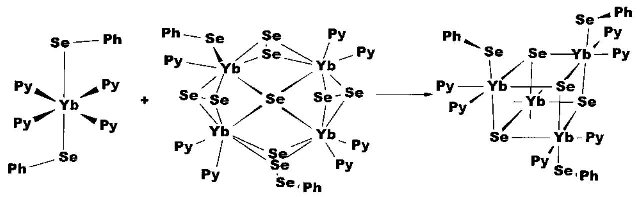
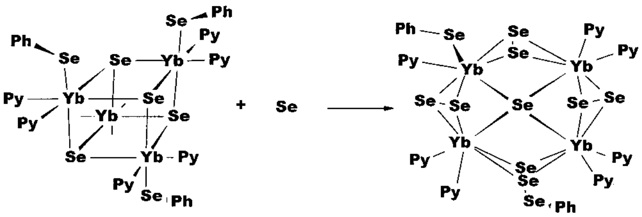
Table 2. Significant Distances (Å) and Angles (deg) for **1**

distances							
Yb(1)−N(1)	2.458(11)	Yb(4)−Se(9)	2.855(2)	Yb(3)−Se(6)	2.857(2)	Yb(2)−Se(2)	2.782(2)
Yb(1)−Se(2)	2.812(2)	Se(4)−Se(5)	2.758(3)	Yb(3)−Se(1)	3.0531(19)	Yb(2)−Se(3)	2.876(2)
Yb(1)−Se(1)	2.851(2)	Se(10)−Se(6)	3.122(3)	Yb(4)−N(7B)	2.47(2)	Yb(3)−N(6)	2.589(12)
Yb(2)−N(2A)	2.49(2)	Se(1A)−Se(12)	2.31(1)	Yb(4)−Se(1)	2.771(2)	Yb(3)−Se(7)	2.871(2)
Yb(2)−Se(5)	2.786(2)	Yb(1)−Se(1A)	2.749(2)	Se(2)−Se(3)	2.390(2)	Yb(4)−N(8)	2.406(12)
Yb(3)−N(4)	2.502(10)	Yb(1)−Se(9)	2.812(2)	Se(6)−Se(7)	2.453(3)	Yb(4)−Se(6)	2.730(2)
Yb(3)−Se(5)	2.787(2)	Yb(2)−N(3)	2.428(13)	Se(10)−Se(8)	3.550(3)	Yb(4)−Se(7)	2.833(2)
Yb(3)−Se(4)	2.882(2)	Yb(2)−Se(4)	2.782(2)	Yb(1)−Se(3)	2.798(2)	Se(4)−Se(10)	2.598(3)
Yb(4)−N(7A)	2.46(2)	Yb(2)−Se(1)	2.799(2)	Yb(1)−Se(8)	2.846(2)	Se(8)−Se(9)	2.392(3)
Yb(4)−Se(8)	2.761(2)	Yb(3)−N(5)	2.559(10)	Yb(2)−N(2B)	2.44(2)	Se(10)−Se(2)	3.604(3)
angles							
N(1)−Yb(1)−Se(1A)	92.2(3)	N(1)−Yb(1)−Se(3)	90.4(3)	N(6)−Yb(3)−Se(5)	87.6(3)	N(4)−Yb(3)−Se(6)	78.4(3)
Se(1A)−Yb(1)−Se(3)	93.01(7)	N(1)−Yb(1)−Se(2)	81.7(3)	N(5)−Yb(3)−Se(6)	124.4(3)	N(6)−Yb(3)−Se(6)	129.8(3)
Se(1A)−Yb(1)−Se(2)	142.56(6)	Se(3)−Yb(1)−Se(2)	50.42(5)	Se(5)−Yb(3)−Se(6)	134.36(6)	N(4)−Yb(3)−Se(7)	93.0(3)
N(1)−Yb(1)−Se(9)	91.3(3)	Se(1A)−Yb(1)−Se(9)	73.58(7)	N(5)−Yb(3)−Se(7)	88.4(3)	N(6)−Yb(3)−Se(7)	86.2(3)
Se(3)−Yb(1)−Se(9)	166.53(5)	Se(2)−Yb(1)−Se(9)	143.01(5)	Se(5)−Yb(3)−Se(7)	173.69(5)	Se(6)−Yb(3)−Se(7)	50.71(6)
N(1)−Yb(1)−Se(8)	86.3(3)	Se(1A)−Yb(1)−Se(8)	123.47(6)	N(4)−Yb(3)−Se(4)	77.7(2)	N(5)−Yb(3)−Se(4)	131.2(3)
Se(3)−Yb(1)−Se(8)	143.45(6)	Se(2)−Yb(1)−Se(8)	93.15(6)	N(6)−Yb(3)−Se(4)	135.6(3)	Se(5)−Yb(3)−Se(4)	58.18(6)
Se(9)−Yb(1)−Se(8)	50.01(6)	N(1)−Yb(1)−Se(1)	170.5(3)	Se(6)−Yb(3)−Se(4)	76.19(6)	Se(7)−Yb(3)−Se(4)	126.78(6)
Se(1A)−Yb(1)−Se(1)	97.29(7)	Se(3)−Yb(1)−Se(1)	89.53(6)	N(4)−Yb(3)−Se(1)	154.6(2)	N(5)−Yb(3)−Se(1)	138.8(3)
Se(2)−Yb(1)−Se(1)	90.90(6)	Se(9)−Yb(1)−Se(1)	90.96(6)	N(6)−Yb(3)−Se(1)	69.8(2)	Se(5)−Yb(3)−Se(1)	89.84(5)
Se(8)−Yb(1)−Se(1)	88.07(6)	N(3)−Yb(2)−N(2B)	87.1(7)	Se(6)−Yb(3)−Se(1)	82.21(6)	Se(7)−Yb(3)−Se(1)	87.28(5)
N(3)−Yb(2)−N(2A)	86.5(8)	N(2B)−Yb(2)−N(2A)	4.2(13)	Se(4)−Yb(3)−Se(1)	81.75(6)	N(8)−Yb(4)−N(7A)	86.3(7)
N(3)−Yb(2)−Se(4)	144.2(2)	N(2B)−Yb(2)−Se(4)	99.5(5)	N(8)−Yb(4)−N(7B)	81.0(9)	N(7A)−Yb(4)−N(7B)	7.4(12)
N(2A)−Yb(2)−Se(4)	97.5(5)	N(3)−Yb(2)−Se(2)	132.1(2)	N(8)−Yb(4)−Se(6)	137.8(3)	N(7A)−Yb(4)−Se(6)	98.2(5)
N(2B)−Yb(2)−Se(2)	84.0(8)	N(2A)−Yb(2)−Se(2)	87.5(8)	N(7B)−Yb(4)−Se(6)	98.7(6)	N(8)−Yb(4)−Se(8)	137.3(3)
Se(4)−Yb(2)−Se(2)	83.68(6)	N(3)−Yb(2)−Se(5)	85.4(2)	N(7A)−Yb(4)−Se(8)	86.8(6)	N(7B)−Yb(4)−Se(8)	94.2(9)
N(2B)−Yb(2)−Se(5)	92.3(8)	N(2A)−Yb(2)−Se(5)	88.2(6)	Se(6)−Yb(4)−Se(8)	84.96(6)	N(8)−Yb(4)−Se(1)	89.3(3)
Se(4)−Yb(2)−Se(5)	59.37(6)	Se(2)−Yb(2)−Se(5)	141.82(5)	N(7A)−Yb(4)−Se(1)	171.4(5)	N(7B)−Yb(4)−Se(1)	170.1(8)
N(3)−Yb(2)−Se(1)	89.2(3)	N(2B)−Yb(2)−Se(1)	171.1(6)	Se(6)−Yb(4)−Se(1)	89.94(6)	Se(8)−Yb(4)−Se(1)	91.40(7)
N(2A)−Yb(2)−Se(1)	174.2(5)	Se(4)−Yb(2)−Se(1)	88.25(6)	N(8)−Yb(4)−Se(7)	85.6(3)	N(7A)−Yb(4)−Se(7)	93.3(6)
Se(2)−Yb(2)−Se(1)	92.60(6)	Se(5)−Yb(2)−Se(1)	95.33(6)	N(7B)−Yb(4)−Se(7)	87.8(7)	Se(6)−Yb(4)−Se(7)	52.28(6)
N(3)−Yb(2)−Se(3)	82.3(2)	N(2B)−Yb(2)−Se(3)	82.6(7)	Se(8)−Yb(4)−Se(7)	136.86(6)	Se(1)−Yb(4)−Se(7)	93.75(6)
N(2A)−Yb(2)−Se(3)	86.6(5)	Se(4)−Yb(2)−Se(3)	133.33(6)	N(8)−Yb(4)−Se(9)	86.9(3)	N(7A)−Yb(4)−Se(9)	80.7(6)
Se(2)−Yb(2)−Se(3)	49.93(5)	Se(5)−Yb(2)−Se(3)	166.86(5)	N(7B)−Yb(4)−Se(9)	85.6(7)	Se(6)−Yb(4)−Se(9)	135.33(6)
Se(1)−Yb(2)−Se(3)	89.01(6)	N(4)−Yb(3)−N(5)	66.6(4)	Se(8)−Yb(4)−Se(9)	50.37(6)	Se(1)−Yb(4)−Se(9)	91.70(6)
N(4)−Yb(3)−N(6)	135.6(3)	N(5)−Yb(3)−N(6)	69.1(3)	Se(7)−Yb(4)−Se(9)	170.71(5)	Se(10)−Se(4)−Se(5)	165.61(7)
N(4)−Yb(3)−Se(5)	92.0(3)	N(5)−Yb(3)−Se(5)	90.0(3)				

Scheme 2



Scheme 3



between Se(10) and Se(6) [3.122(3) Å] is shorter than the bonds between Se(10) and either Se(2) [3.604(3) Å] or Se(8) [3.550(3) Å].

Cluster **1** crystallizes in a compositionally disordered structure with a minor component (38%) containing an additional Se atom inserted into the terminal Yb−Se(Ph) bond to give a SeSePh ligand part of the time (Figure 1; Se1A bonds to Se12). In the structure, one of the lattice solvents is disordered between two positions that reflect the steric demands imposed by this additional Se. Changing the amount of Se in the initial reaction 1 stoichiometry from $x = 9$ to 6 affects only the yield of the final product and not the product identity or relative percentages in the compositional disorder.

The diselenide linkages in **1** are readily reduced upon addition of $(py)_4Yb(SePh)_2$ to give the cubane cluster $(py)_8Yb_4Se_4(SePh)_4$ (reaction 2, Scheme 2). Conversely, reduction of elemental Se

$$\mathbf{1} + 5Yb(SePh)_2 \rightarrow [(py)_2YbSe(SePh)]_4 + PhSeSePh \quad (2)$$

by oxidation of the selenido ligands is also facile: the (SeSe) ligands in **1** can also be regenerated by the reaction of the cubane with elemental Se in pyridine at room temperature (reaction 3, Scheme 3).

$$(py)_8Yb_4Se_4(SePh)_4 + 5Se \rightarrow (py)_8Yb_4Se(SeSe)_3(SeSeSePh)(Se_{0.38}SePh) \quad (3)$$

With PhTeTePh, an analogous Se-rich tellurolate derivative $(py)_8Yb_4Se(SeSe)_3(SeSeTePh)(SeTePh)$ (**2**) is isolated (reaction 4, Scheme 4), and the structure of **2** is found to be isomorphous with **1**, with the only significant difference being the elimination of the compositional disorder (Figure 2) resulting from complete insertion of Se into the terminal Ln−Te(Ph) bond. Table 3 gives a list of significant bond lengths and angles for **2**. As in **1**, one of the chalcogenolate ligands in **2** has been displaced from a Yb(III) ion and now coordinates clearly to a single SeSe unit, with a Te(1)−Se(5) distance of 2.694(3) Å. Of the remaining three SeSe ligands in the structure, Se(6)−Se(7) has both the longest SeSe bond (2.435(4) Å) and closest contact to the TePh ligand [Te(1)−Se(7), 3.222(3) Å]. In contrast with **1**, however,

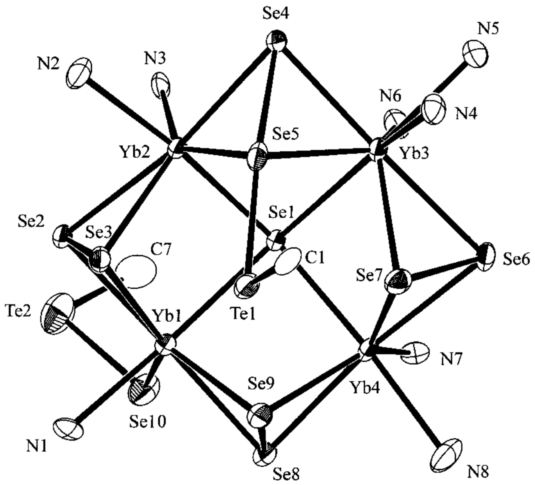
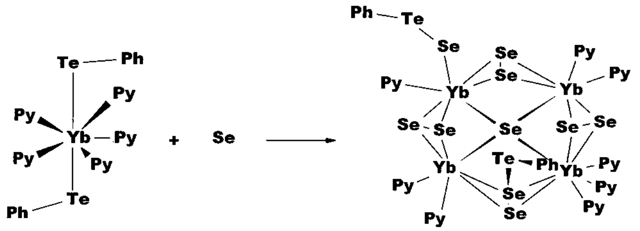
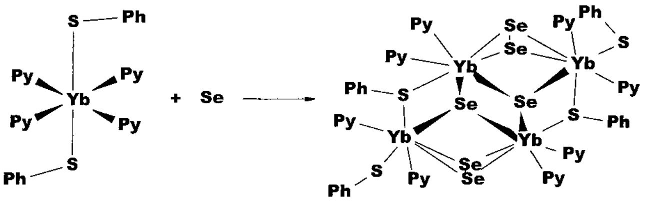


Figure 2. Core bonding region of the molecular structure of (py)$_8$Yb$_4$Se(SeSe)$_3$(SeSeTePh)(SeTePh) (**2**) with the C and H atoms removed. Thermal ellipsoids are drawn at the 50% probability level.

Scheme 4



Scheme 5



the second chalcogenolate (TePh) ligand is also not coordinated to the Ln because of complete insertion of Se to give the terminal η^1-SeTePh ligand. The Te(2)–Se(10) bond length [2.504(3) Å] in the terminal ligand provides a convenient benchmark for evaluating the weaker Se–Te bonds in the structure.

$$4\text{Yb} + 9\text{Se} + \text{PhTeTePh} \rightarrow (\text{py})_8\text{Yb}_4\text{Se}(\text{SeSe})_3(\text{SeSeTePh})(\text{SeTePh}) \quad (4)$$

With benzenethiolate starting materials a completely different tetrametallic structure is observed. Addition of excess Se still results in the formation of a chalcogen-rich compound with SeSe ligands, but in this case the final cluster product is the relatively chalcogen poor (py)$_8$Yb$_4$(μ_3-Se)$_2$(μ_2-SeSe)$_2$(μ_2-SPh)$_2$(SPh)$_2$ (**3**) (reaction 5, Scheme 5). The structure of **3**, as determined by low-temperature single-crystal diffraction, is a rhomboid array

$$\text{Yb} + \text{PhSSPh} + 6\text{-}9\ \text{Se} \rightarrow (\text{py})_8\text{Yb}_4(\mu_3\text{-Se})_2(\mu_2\text{-SeSe})_2(\mu_2\text{-SPh})_2(\text{SPh})_2 \quad (5)$$

of Yb(III) ions with the edges spanned by alternating pairs of μ_2-SPh and μ_2-SeSe ligands (Figure 3). The top and bottom of the rhombus are capped by μ_3-Se^{2-} ligands, and there are two terminal thiolate ligands coordinated to opposite Yb(III) ions. Chemically inequivalent Yb(1) and Yb(2) are both seven coordinate, but Yb(1) has bonds to two Se^{2-} ligands, while Yb(2) coordinates a terminal thiolate and only one Se^{2-}. Table 4 gives a listing of significant bond lengths and angles for **3**. There are two crystallographically related SeSe ligands with 2.357(2) Å Se–Se bond lengths, and there are no SeSe·S(Ph) interactions. As found in the synthesis of **1**, cluster **3** is the only isolable product of this reaction, even when a large excess of Se is present.

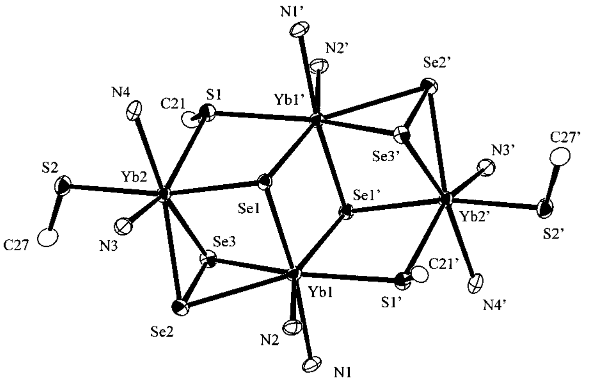


Figure 3. Core bonding region of the molecular structure of (pyridine)$_8$Yb$_4$(SeSe)$_2$(Se)$_2$(μ_2-SPh)$_2$(SPh)$_2$ (**3**) with the C and H atoms removed. Thermal ellipsoids are drawn at the 50% probability level.

Discussion

This work, which outlines the synthesis and characterization of Se-rich Ln clusters, contains a number of significant observations. First, the dramatic variations in the structures of **1**–**3** are clearly related to the identity of ancillary ligands, and as such provide insight into the factors that govern cluster formation. Second, because we now have crystalline systems for both chalcogenido clusters and chalcogen-rich materials with the same combination of Ln, E, EPh, and coordinated Lewis base, we can chemically probe the nature of cluster stability, i.e., whether lanthanides form more stable complexes with E^{2-} or EE^{2-} ligands. Finally, the isolation and characterization of a lanthanide compound with an EEPh ligand has implications for understanding the process by which Ln(EPh)$_x$ molecules react with E to give cluster compounds.

The importance of ancillary ligands in determining the structure of a cluster product is readily apparent from an analysis of the molecular structures of **1**–**3**. The extent of Se reduction/EPh oxidation depends on the strength of the Ln–E(Ph) bond. Additional Se does not result in further displacement of thiolate, and once isolated, **3** is unstable with respect to deposition of elemental Se. There is greater displacement of EPh ligand in **1**, and this trend is maximized in the TePh compound **2**, where all Ln–E(Ph) bonds have been disrupted.

In previous Ln cluster chemistry, only Ln ion size played a significant role in structure determination. Of the sulfido and selenido clusters previously reported, the early Ln (Ce–Er) all readily crystallize as octanuclear products,[7a–d] with a cube of 8 Ln connected on the cube faces with E^{2-} ligands and along the cube edges with EPh ligands. The Ln$_8$ structure appears to be particularly stable, with all combinations of S^{2-}/Se^{2-} and SPh/SePh ligands giving the same cubic arrangement, although in a multitude of crystal packing motifs. The smaller Ln form derivatives of the cubane structure[7e] with octahedral Ln(III) coordination environments.

In the present system, the strength of the Ln–E(Ph) bond appears to influence structure significantly. Although Ln–E(Ph) bond strengths have never been measured, it is reasonable to

Table 3. Significant Distances (Å) and Angles (deg) for **2**

distances							
Yb(1)−N(1)	2.48(2)	Se(5)−Te(1)	2.694(3)	Yb(3)−Se(7)	2.880(3)	Yb(2)−Se(5)	2.796(3)
Yb(1)−Se(8)	2.814(3)	Se(5)−Se(4)	2.853(4)	Yb(4)−N(7)	2.41(2)	Yb(3)−N(4)	2.52(2)
Yb(1)−Se(1)	2.852(3)	Te(1)−Se(3)	3.591(3)	Yb(4)−Se(9)	2.762(3)	Yb(3)−Se(4)	2.780(3)
Yb(2)−Se(4)	2.765(3)	Te(2)−C(7)	2.08(3)	Yb(4)−Se(8)	2.857(3)	Yb(3)−Se(5)	2.905(3)
Yb(2)−Se(1)	2.802(3)	Yb(1)−Se(10)	2.760(3)	Se(6)−Se(7)	2.453(4)	Yb(4)−N(8)	2.48(2)
Yb(3)−N(5)	2.55(2)	Yb(1)−Se(3)	2.828(3)	Te(1)−Se(7)	3.222(3)	Yb(4)−Se(1)	2.780(3)
Yb(3)−Se(6)	2.878(3)	Yb(2)−N(3)	2.44(2)	Te(1)−C(1)	2.12(2)	Se(2)−Se(3)	2.395(4)
Yb(3)−Se(1)	3.054(3)	Yb(2)−Se(3)	2.787(3)	Yb(1)−Se(2)	2.802(3)	Se(8)−Se(9)	2.395(4)
Yb(4)−Se(7)	2.732(3)	Yb(2)−Se(2)	2.878(3)	Yb(1)−Se(9)	2.846(3)	Te(1)−Se(9)	3.489(3)
Yb(4)−Se(6)	2.839(3)	Yb(3)−N(6)	2.58(2)	Yb(2)−N(2)	2.46(2)	Se(10)−Te(2)	2.504(3)
angles							
N(1)−Yb(1)−Se(10)	88.7(4)	N(1)−Yb(1)−Se(2)	90.3(4)	N(5)−Yb(3)−Se(4)	88.0(4)	N(6)−Yb(3)−Se(4)	87.9(4)
Se(10)−Yb(1)−Se(2)	92.10(9)	N(1)−Yb(1)−Se(8)	93.3(4)	N(4)−Yb(3)−Se(6)	92.4(4)	N(5)−Yb(3)−Se(6)	89.3(4)
Se(10)−Yb(1)−Se(8)	72.96(9)	Se(2)−Yb(1)−Se(8)	164.54(8)	N(6)−Yb(3)−Se(6)	84.6(4)	Se(4)−Yb(3)−Se(6)	172.52(8)
N(1)−Yb(1)−Se(3)	81.5(4)	Se(10)−Yb(1)−Se(3)	140.74(8)	N(4)−Yb(3)−Se(7)	77.6(5)	N(5)−Yb(3)−Se(7)	124.6(4)
Se(2)−Yb(1)−Se(3)	50.35(8)	Se(8)−Yb(1)−Se(3)	145.10(8)	N(6)−Yb(3)−Se(7)	127.9(4)	Se(4)−Yb(3)−Se(7)	136.14(8)
N(1)−Yb(1)−Se(9)	87.7(4)	Se(10)−Yb(1)−Se(9)	122.53(8)	Se(6)−Yb(3)−Se(7)	50.43(8)	N(4)−Yb(3)−Se(5)	77.1(4)
Se(2)−Yb(1)−Se(9)	145.23(8)	Se(8)−Yb(1)−Se(9)	50.06(8)	N(5)−Yb(3)−Se(5)	130.1(5)	N(6)−Yb(3)−Se(5)	137.1(4)
Se(3)−Yb(1)−Se(9)	95.12(8)	N(1)−Yb(1)−Se(1)	170.7(4)	Se(4)−Yb(3)−Se(5)	60.19(9)	Se(6)−Yb(3)−Se(5)	126.30(9)
Se(10)−Yb(1)−Se(1)	100.52(9)	Se(2)−Yb(1)−Se(1)	88.44(8)	Se(7)−Yb(3)−Se(5)	75.96(8)	N(4)−Yb(3)−Se(1)	153.8(5)
Se(8)−Yb(1)−Se(1)	90.38(8)	Se(3)−Yb(1)−Se(1)	90.65(8)	N(5)−Yb(3)−Se(1)	139.6(5)	N(6)−Yb(3)−Se(1)	69.4(4)
Se(9)−Yb(1)−Se(1)	88.08(8)	N(3)−Yb(2)−N(2)	86.8(6)	Se(4)−Yb(3)−Se(1)	89.71(7)	Se(6)−Yb(3)−Se(1)	87.83(8)
N(3)−Yb(2)−Se(4)	84.5(4)	N(2)−Yb(2)−Se(4)	90.3(5)	Se(7)−Yb(3)−Se(1)	82.47(8)	Se(5)−Yb(3)−Se(1)	81.64(8)
N(3)−Yb(2)−Se(3)	131.8(4)	N(2)−Yb(2)−Se(3)	84.5(5)	N(7)−Yb(4)−N(8)	82.1(7)	N(7)−Yb(4)−Se(7)	138.0(4)
Se(4)−Yb(2)−Se(3)	142.70(8)	N(3)−Yb(2)−Se(5)	145.9(4)	N(8)−Yb(4)−Se(7)	99.5(5)	N(7)−Yb(4)−Se(9)	137.4(4)
N(2)−Yb(2)−Se(5)	97.0(5)	Se(4)−Yb(2)−Se(5)	61.73(8)	N(8)−Yb(4)−Se(9)	90.8(5)	Se(7)−Yb(4)−Se(9)	84.58(9)
Se(3)−Yb(2)−Se(5)	82.24(8)	N(3)−Yb(2)−Se(1)	90.9(4)	N(7)−Yb(4)−Se(1)	89.8(4)	N(8)−Yb(4)−Se(1)	170.0(5)
N(2)−Yb(2)−Se(1)	173.6(4)	Se(4)−Yb(2)−Se(1)	95.47(8)	Se(7)−Yb(4)−Se(1)	90.48(8)	Se(9)−Yb(4)−Se(1)	91.24(9)
Se(3)−Yb(2)−Se(1)	92.55(8)	Se(5)−Yb(2)−Se(1)	88.23(9)	N(7)−Yb(4)−Se(6)	85.9(4)	N(8)−Yb(4)−Se(6)	91.1(5)
N(3)−Yb(2)−Se(2)	82.2(4)	N(2)−Yb(2)−Se(2)	85.8(5)	Se(7)−Yb(4)−Se(6)	52.20(8)	Se(9)−Yb(4)−Se(6)	136.41(9)
Se(4)−Yb(2)−Se(2)	166.29(8)	Se(3)−Yb(2)−Se(2)	49.99(8)	Se(1)−Yb(4)−Se(6)	94.19(8)	N(7)−Yb(4)−Se(8)	87.0(4)
Se(5)−Yb(2)−Se(2)	131.79(9)	Se(1)−Yb(2)−Se(2)	87.91(8)	N(8)−Yb(4)−Se(8)	82.8(5)	Se(7)−Yb(4)−Se(8)	135.00(9)
N(4)−Yb(3)−N(5)	66.6(6)	N(4)−Yb(3)−N(6)	136.7(6)	Se(9)−Yb(4)−Se(8)	50.42(8)	Se(1)−Yb(4)−Se(8)	90.95(8)
N(5)−Yb(3)−N(6)	70.2(6)	N(4)−Yb(3)−Se(4)	92.9(4)	Se(6)−Yb(4)−Se(8)	171.20(7)		

Table 4. Significant Distances (Å) and Angles (deg) for **3**[a]

distances							
Yb(1)−N(1)	2.486(6)	S(1)−C(21)	1.788(8)	Yb(2)−S(1)	2.735(2)	Yb(1)−Se(1)′	2.835(2)
Yb(1)−S(1)′	2.785(3)	Yb(1)−N(2)	2.504(6)	Yb(2)−Se(2)	2.861(2)	Yb(2)−N(4)	2.513(6)
Yb(1)−Se(2)	2.898(2)	Yb(1)−Se(3)	2.829(2)	S(2)−C(27)	1.753(8)	Yb(2)−Se(1)	2.755(2)
Yb(2)−S(2)	2.678(3)	Yb(2)−N(3)	2.509(6)	Yb(1)−Se(1)	2.779(2)	Se(2)−Se(3)	2.357(2)
Yb(2)−Se(3)	2.830(2)						
angles							
N(1)−Yb(1)−N(2)	81.1(2)	N(1)−Yb(1)−Se(1)	170.43(15)	N(3)−Yb(2)−S(2)	89.63(15)	N(4)−Yb(2)−S(2)	81.01(15)
N(2)−Yb(1)−Se(1)	90.68(15)	N(1)−Yb(1)−S(1)′	82.15(15)	N(3)−Yb(2)−S(1)	149.48(15)	N(4)−Yb(2)−S(1)	75.92(15)
N(2)−Yb(1)−S(1)′	76.46(15)	Se(1)−Yb(1)−S(1)′	100.80(7)	S(2)−Yb(2)−S(1)	94.96(8)	N(3)−Yb(2)−Se(1)	90.51(15)
N(1)−Yb(1)−Se(3)	89.99(15)	N(2)−Yb(1)−Se(3)	127.87(15)	N(4)−Yb(2)−Se(1)	88.03(15)	S(2)−Yb(2)−Se(1)	168.62(5)
Se(1)−Yb(1)−Se(3)	91.20(7)	S(1)′−Yb(1)−Se(3)	153.07(5)	S(1)−Yb(2)−Se(1)	79.29(7)	N(3)−Yb(2)−Se(3)	126.46(15)
N(1)−Yb(1)−Se(1)′	98.01(15)	N(2)−Yb(1)−Se(1)′	153.40(14)	N(4)−Yb(2)−Se(3)	158.49(14)	S(2)−Yb(2)−Se(3)	97.39(8)
Se(1)−Yb(1)−Se(1)′	91.53(6)	S(1)′−Yb(1)−Se(1)′	77.09(6)	S(1)−Yb(2)−Se(3)	82.89(7)	Se(1)−Yb(2)−Se(3)	91.67(6)
Se(3)−Yb(1)−Se(1)′	78.58(6)	N(1)−Yb(1)−Se(2)	85.28(15)	N(3)−Yb(2)−Se(2)	77.62(15)	N(4)−Yb(2)−Se(2)	152.54(14)
N(2)−Yb(1)−Se(2)	79.43(15)	Se(1)−Yb(1)−Se(2)	88.39(6)	S(2)−Yb(2)−Se(2)	101.52(7)	S(1)−Yb(2)−Se(2)	130.36(6)
S(1)′−Yb(1)−Se(2)	154.22(5)	Se(3)−Yb(1)−Se(2)	48.57(5)	Se(1)−Yb(2)−Se(2)	89.61(6)	Se(3)−Yb(2)−Se(2)	48.92(5)
Se(1)′−Yb(1)−Se(2)	127.13(5)	N(3)−Yb(2)−N(4)	75.0(2)				

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

assume that Ln−E bond strengths would decrease as the size of the chalcogen increases, i.e., Ln−S > Ln−Se > Ln−Te, based on gas-phase diatomic bond strengths[14] and limited chemical reactivity studies.[7d] The thiolate compound **3** differs dramatically from **1** and **2** in three ways. First, SPh is less readily eliminated from the Ln coordination sphere than are SePh or TePh, and a final product with a 1:1 Ln:EPh ratio is obtained. Second, in this structure, all the SPh remain coordinated to the Ln, with half of these bridging two Yb, even in the presence of strong pyridine donor ligands. Finally, there is no evidence of any Ln−Se−S−Ph connectivity. All of these differences can readily be attributed to the relative strength of the Ln−S bond.

With the weaker Ln−Se(Ph) bonds in **1**, there are fewer SePh ligands in the final product, and of the two that remain, only one coordinates to Yb in a terminal bonding mode. The second SePh is displaced from the primary coordination sphere by a neutral pyridine donor, and instead coordinates one (SeSe)$^{2-}$ ligand to give an (SeSeSePh)$^{3-}$ ligand. In this structure there is also a compositional disorder at the terminal SePh site, in which 38% of the product has an additional Se inserted into the Yb−Se(Ph) bond to give a terminal SeSePh functional group.

Direct bonds between Ln and Te are the weakest of the chalcogen group, and this is reflected clearly in the structure of **2**, in which all direct interactions between Ln and Te have been eliminated. Once again, one of the tellurolates has been displaced

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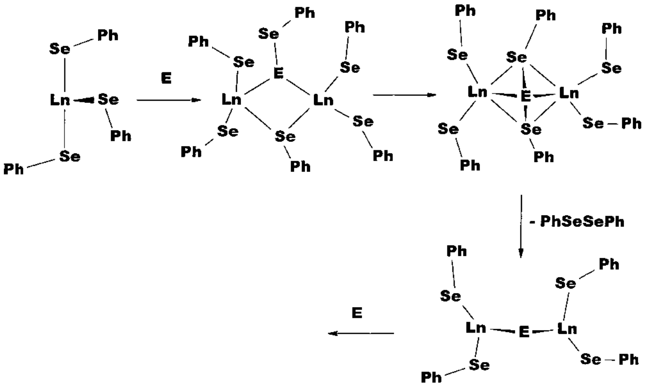
Scheme 6



by a neutral pyridine donor, and this displaced TePh again attaches to a SeSe unit to form a $(SeSeTePh)^{3-}$ ligand. Of the two isomorphous materials **1** and **2**, the Se−Se(EPh) bond elongation in **2** is greater, by 0.1 Å, than the corresponding elongation in **1**. This bonding, which is directly parallel with the structural chemistry of polyiodide compounds,[15] is rationalized in localized, hypervalent terms.[16]

More significantly, the second TePh has also been displaced from the primary Ln coordination sphere by insertion of a Se atom, to form a terminal SeTePh moiety. This reactivity is presumably motivated by the formation of the stronger Ln−Se bond, but there may also be a contribution from the fact that insertion of Se effectively distances the Ph fragment from the inner coordination sphere, and this reduces ligand−ligand repulsions. Chalcogen insertion presumably represents the first step in the reactions that generate chalcogenido clusters from chalcogenolate compounds. Insertion of E′ into an Ln−E(Ph) bond could be followed by coordination of a second EPh to the metal ligated chalcogen E(E′Ph), and this would then set the stage for oxidative elimination of PhE′E′Ph and the formation of a chalcogenido ligand (Scheme 6).

We had initially investigated the reactions of $Ln(EPh)_3$ with E because we expected to form these $Ln(-E\text{-}E'\text{-}Ph)_3$ compounds, which we hoped could then be reduced by elemental Ln to form chalcogenido clusters. Fortunately, we overlooked the facility by which EE bonds rearrange and underestimated the tendency to form highly charged anions in Ln chemistry. Chalcogen reduction is considerably more facile than had been initially expected, and the initial insertion product had never been observed prior to this work. Even in the all-selenium cluster **1** there is clear crystallographic evidence for the formation of a terminal SeSePh ligand, which cocrystallizes (38%) along with the terminal SePh product. In this case, however, there is less of a thermodynamic driving force to the reaction, because there is no gain in Ln−E bond strength.

It is important to note that the percentage of cocrystallization product cannot simply be controlled by the amount of elemental Se in the reaction. In an attempt to determine whether the rhombohedral core of **3** could be generated with Se/SeSe/SePh ligands, reaction 1 was examined with $x = 6$ rather than $x = 9$ equivalents of Se. An analysis of the final product identified the same SePh/SeSePh cocrystallized structure, **1**, albeit in a considerably lower yield.

Chemical interconversion of cluster compounds with E^{2-} and $(EE)^{2-}$ ligands is facile. The Se-rich cluster **1** is reduced by $Yb(SePh)_2$ to give the Yb_4Se_4 cubane cluster (Scheme 2), and this cubane reacts with elemental Se to give back cluster **1** (Scheme 3). These experiments indicate that Ln/E stoichiometry is the important factor determining whether a chalcogenido cluster or a chalcogen-rich material is the final product in these displacement reactions. The relative stability of Ln clusters with EE ligands was first inferred from our isolation of $(THF)_6Yb_4I_2S(SS)_4$, but cluster interconversion experiments to establish the kinetic or thermodynamic nature of these products were impossible at the time. Related work with Cp* ligand systems [dimeric $(Cp^*{}_2Ln)_2(Se_x)$][17] has also suggested Ln compounds with SeSe ligands are readily prepared, but there are no clear reactivity studies due to the tendency of these systems to disproportionate, as found in the synthesis of $(Cp^*Sm)_6Se_{11}$.[18] With the present compounds, it is clear that in the reactions of E with $Ln(EPh)_3$ the first equivalent of chalcogen will be reduced to E^{2-}, with oxidative elimination of PhEEPh. This E^{2-} reacts further with additional elemental E to give compounds with EE ligands, in which the anionic electron density in this relatively electropositive ligand is effectively decentralized.

Conclusion

Lanthanide clusters with SeSe ligands are readily prepared, either by direct combination of the elements or by reaction of Ln_4Se_4 cubane clusters with elemental Se. These SeSe ligands are also reactive, and can be reduced to give Ln clusters with Se^{2-} ligands. Ancillary ligands have a significant impact on the structure of the final product, and this influence can be attributed directly to the relative strengths of Ln−E bonds. With Se/TePh ligands, the first example of a Ln compound with a terminal Ln-E-E′Ph functional group has been obtained.

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Supporting Information Available: X-ray crystallographic files for the crystal structures of **1**−**3** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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