Pyridine Coordination Complexes of the Divalent Ytterbium Chalcogenolates $Yb(EPh)_2$ (E = S, Se, Te)

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Chalcogenolate complexes of ytterbium can be prepared *via* a number of synthetic approaches. The reaction between Yb metal and PhE–EPh (E = S, Se, Te) in liquid ammonia results in the formation of divalent ytterbium chalcogenolates, which can be isolated as the pyridine coordination complexes $(pyridine)_4Yb(SC_6H_5)_2$ (**1**) $(pyridine)_4Yb(SeC_6H_5)_2$ (**2**), and $(pyridine)_5Yb(TeC_6H_5)_2$ (**3**). Reaction of $YbCl_3$ with 3 equiv of NaTePh results in the reduction of the metal and the formation of **3** and diphenyl ditelluride. The thiolate **1** and selenolate **2** can be prepared by reducing the corresponding dichalcogenide with a ytterbium/mercury amalgam in THF. All three ytterbium complexes have been characterized by elemental analysis and by NMR, IR, and UV–visible spectroscopy. The visible spectra were found to be concentration dependent. All three complexes have also been characterized by single-crystal X-ray diffraction and shown to be molecular, with *trans* phenylchacogenolate ligands. Octahedral **1** crystallizes in the triclinic space group $P\bar{1}$, with $a = 8.797(3)$ Å, $b = 9.412(4)$ Å, $c = 9.947(7)$ Å, $\alpha = 87.07(4)°$, $\beta = 66.79(4)°$, $\gamma = 75.25(3)°$, $V = 730.9(7)$ Å^3, $Z = 1$, and $\rho_{calc} = 1.608$ g/cm^3 (Mo Kα radiation at −115 °C). Octahedral **2** crystallizes in the space group $C2/c$, with $a = 25.670$Å(6) Å, $b = 9.027(4)$ Å, $c = 17.680(3)$ Å, $\beta = 133.62(2)°$, $V = 2966(2)$ Å^3, $Z = 4$, $\rho_{calc} = 1.795$g/cm^3 (Mo Kα radiation at −120 °C). The pentagonal bipyramid **3** crystallizes in the space group *Pbca*, with $a = 13.695(9)$ Å, $b = 16.422(8)$ Å, $c = 31.917(7)$ Å, $V = 7178(6)$ Å^3, $Z = 8$, $\rho_{calc} = 1.83$ g/cm^3 (Mo Kα radiation at −120 °C). The metal–chalcogenide bond lengths in all three structures can be predicted with the summation of ionic radii.

Introduction

The synthesis of solid-state compounds from molecular precursors has been the subject of intense interest, and there have been numerous reports detailing the synthesis of transition metal chalcogenolate complexes for use in thermolysis experiments.[1] These compounds have been used to prepare metastable forms of solid-state chalcogenides such as thin films or nanometer-sized clusters. The emerging interest in incorporating lanthanide elements in the covalent II–VI or III–V semiconductors[2] has led to a number of reports describing the synthesis and characterization of rare earth metal chalcogenolates.[3] In rare earth metal chalcogenolate chemistry, the tendency of chalcogenolate ligands to span more than one metal center, combined with the tendency of the rare earth metal ions to maximize coordination numbers, generally leads to the formation of polymetallic species[3c–e,4] unless the metal coordination sphere is saturated with multidentate[3b] or sterically demanding ligands.[3a,5]

In this paper we describe a number of synthetic approaches to molecular pyridine coordination complexes of the ytterbium chalcogenolates $(pyridine)_4Yb(SC_6H_5)_2$, $(pyridine)_4Yb(SeC_6H_5)_2$, and $(pyridine)_5Yb(TeC_6H_5)_2$. The complexes are all intensely colored, and the lowest energy optical absorptions are interpreted in terms of metal to pyridine charge-transfer excitations. We report the molecular structures of all three compounds and show that the metal–chalcogenide bond length can be described in terms of ionic radius summations.

Experimental Section

General Procedures. 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 sodium/benzophenone and collected immediately prior to use. $YbCl_3$, Yb (Strem), anhydrous pyridine, superhydride (Aldrich), and ammonia (Matheson) were purchased and used as received. Ph_2S_2 and Ph_2Se_2 were purchased from Aldrich and recrystallized twice from hexane. PhTeTePh was prepared according to the literature procedure.[6] Melting points were taken in sealed capillaries and are uncorrected. IR spectra of the compounds in a Nujol mull were taken on a Mattus Cygnus 100 FTIR spectrometer and recorded from 4000 to 450 cm^{-1}. NMR spectra were recorded on a Varian XL 200-MHz instrument at 24.5 °C, with chemical shifts reported in units of δ relative to solvent. 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 preformed by Quantitative Technologies, Inc. (Salem NJ).

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Synthesis of (pyridine)$_4$Yb(SC$_6$H$_5$)$_2$. From Yb Metal. Ytterbium powder (534 mg, 3.00 mmol) and diphenyl disulfide (672 mg, 3.10 mmol) were dissolved in liquid ammonia (150 mL), and the solution was stirred in an acetone/dry ice bath, giving a blue mixture. The blue color dissipated, and a yellow mixture was formed. After 6 h of stirring at −50 °C, the yellow reaction mixture was slowly brought to room temperature. After 3 h, a red solid remained. The last traces of ammonia were removed by vacuum. The solid was washed with hexane (2 × 20 mL). Pyridine (40 mL) was added to the solid, giving a dark purple solution. The mixture was stirred and filtered, and the filtrate was cooled to give black (green) crystals (0.81 g, 37%) mp = 164–166 °C dec. Anal. Calcd for $C_{32}H_{30}N_4S_2Yb$: C, 54.3; H, 4.28; N, 7.92. Found: C, 52.8; H, 4.22; N, 7.97. UV (in pyridine): λ_{max} = 302 and 577 nm. IR: 1594 (m), 1577 (m), 1231 (s), 1154 (m), 952 (w), 722 (s), 701 cm^{-1} (m). The ^{1}H NMR spectrum (25 mg in 0.60 mL of THF-d_8) contained only three resonances at δ 8.54, 7.65, and 7.26, while the ^{13}C NMR spectrum contained resonances at δ 150.8, 136.3, 129.7, 125.8, and 124.3.

From Yb/Hg Amalgam. An amalgam of Hg/Yb was prepared by adding Yb (241 mg, 1.4 mmol) to mercury (4.2 g, 20 mmol). Diphenyl disulfide (302 mg, 1.4 mmol) and THF (40 mL) were added to the amalgam, and a yellow solution color developed within seconds. After 2 days of stirring, the solution was dark red, and a yellow precipitate formed. The reaction mixture was allowed to stir for 4 days more,after which it was taken to dryness and the residue was dissolved in pyridine. The resulting mixture was filtered, and the filtrate was cooled to give dark crystals (324 mg, 32.6%), which were identified by melting point and by NMR and UV–visible spectroscopy.

Synthesis of (pyridine)$_4$Yb(SeC$_6$H$_5$)$_2$. From Yb Metal. Ytterbium powder (0.537 g, 3.10 mmol) was dissolved in liquid ammonia (15 mL), and the solution was stirred in a 2-propanol/dry ice bath. To this dark blue solution was added with stirring diphenyl diselenide (1.451 g, 4.65 mmol). The blue color disappeared immediately, the solution turned yellow, and a dark yellow precipitate formed. The reaction mixture was stirred in the dry ice bath for 1 h and then allowed to warm over 1 h, after which the last traces of ammonia were removed by vacuum. As the solid reached room temperature, the color changed from dark yellow to pale red. The red material was washed with hexanes (2 × 25 mL) to remove unreacted diphenyl diselenide, which was recovered by evaporation (1.48 mmol, 0.475 g). Pyridine (20 mL) was added to the red material, and an intensely dark violet color formed immediately; this solution was filtered, and the filtrate was cooled to yield black (dark green) needles (1.20 g, 48%), mp 99–100 °C dec. Anal. Calcd for $C_{32}H_{30}N_4Se_2Yb$: C, 47.9; H, 3.74; N, 6.99. Found: C, 47.5; H, 3.85; N, 7.42. Found after 5 days: C, 41.2; H, 3.20; N, 4.77. Found after 3 weeks: C, 35.4; H, 2.67; N, 2.72. UV (ca. 2 mg/mL): λ_{max} = 307 and 552 nm. The ^{1}H NMR spectrum of a sample in THF-d_8 showed resonances at δ 8.58, 7.61, 7.54, 7.30 and 7.26, and 6.88. The NMR spectrum is solvent dependent; in pyridine-d_5 there are two nonsolvent resonances at δ 8.05 and 7.10, but overlap with solvent precludes integration. IR: 1620 (w), 1594 (s), 1571 (s), 1483 (s), 1483 (s), 1467 (s), 1440 (s), 1378 (m), 1217 (m), 1149 (m), 1032 (s), 1021 (m), 999 (m), 753 (m), 733 (s), 700 (s), 666 (m), 618 (m), 470 cm^{-1} (m).

From Yb/Hg Amalgam. Mercury (3.0 g, 15 mmol) and ytterbium powder (0.52 g, 3.0 mmol) were stirred together until an amalgam formed. Diphenyl diselenide (0.94 g, 3 mmol) was dissolved in THF (60 mL), and this solution was added to the Hg/Yb amalgam. A yellow precipitate formed within 1 h. The reaction mixture was stirred for 3 days and then concentrated to dryness. Pyridine (20 mL) was added, and the solution was brought to 90 °C . After cooling to room temperature, the deep purple solution was filtered and the filtrate was cooled further (−20 °C) to give dark crystals (1.1 g, 45%), which were collected and identified by melting point and UV–visible spectroscopy.

Synthesis of (pyridine)$_5$Yb(TeC$_6$H$_5$)$_2$. From YbCl$_3$. A solution of diphenyl ditelluride (1.23 g 3.00 mmol) in diethyl ether (10 mL) was treated dropwise with sodium triethylborohydride (6 mL of a 1 M solution, 6.00 mmol) in THF. The reaction mixture was stirred for 4 h and evaporated to dryness. The colorless solid was washed with hexane (2 × 10 mL), pumped to dryness, and then treated with a solution of YbCl$_3$-(0.556 g, 2.00 mmol) in THF (20 mL). The solution was stirred for 6 h and filtered, the filtrate was evaporated to dryness, and the residue was washed with diethyl ether (2 × 10 mL). The dark red product was redissolved in pyridine (15 mL), the solution was filtered, and the filtrate was layered with diethyl ether to yield black (dark red) crystals (0.250 g, 13%), mp 248–250 °C dec. Diphenyl ditelluride (0.39 g, 0.95 mmol) was recovered from the supernatant by taking the filtrate to dryness and extracting with hexane. As found in the chemistry of europium(II),[3d] these Yb(II) crystals rapidly desolvate to approach a stoichiometry of (pyridine)Yb(TePh)$_2$. Anal. Calcd for $C_{17}H_{15}NTe_2Yb$: C, 30.4; H, 2.37; N, 2.20. Found: C, 30.2; H, 2.40; N, 2.84. IR: 1595 (m), 1567 (m), 1484 (w), 1465 (s), 1439 (s), 1378 (w), 1215 (w), 1147 (w), 1065 (m), 1035 (m), 1014 (m), 1002 (m), 752 (m), 731 (s), 701 (s), 650 (w), 620 (m), 457 cm^{-1} (m). UV (ca. 2 mg/mL in pyridine): λ_{max} = 391 and 525 nm. The ^{1}H NMR spectrum (20 mg in 0.50 mL of THF-d_8) contained resonances at δ 8.59, 7.69, 7.30 (a doublet superimposed on a broader resonance), 6.95, and 6.82. At this concentration, a dark orange solid precipitated within minutes in the NMR tube. Crystals suitable for X-ray diffraction were obtained by isolation from the supernatant within 1 h of crystallization and immediately cooling the sample to −100 °C. X-ray powder diffraction of a 3-day-old sample gave no measurable diffraction intensity.

From Yb Metal. Ytterbium powder (2.0 mmol, 0.346 g) was dissolved in liquid ammonia (15 mL), and the solution was stirred magnetically in a 2-propanol/dry ice bath. To this dark blue solution was added with stirring diphenyl ditelluride (2.0 mmol, 0.820 g). The blue color disappeared immediately, the solution turned red, and a dark violet precipitate formed. The reaction mixture was stirred in the dry ice bath for 15 min and then allowed to warm up over 1 h, after which the last traces of ammonia were removed by vacuum. The purple material was washed with hexane (2 × 25 mL) to remove unreacted diphenyl ditelluride; only trace amounts were recovered by evaporation. Pyridine (40 mL) was added, and the purple solid slowly dissolved. The dark red solution was filtered, and the filtrate was layered with diethyl ether to yield dark red microcrystals that had the same melting point and UV–visible spectrum as the material isolated from the metathesis reaction.

X-ray Structure Determinations of 1–3. Data for **1**–**3** were collected on a CAD4 diffractometer with Mo Kα radiation (λ = 0.710 73 Å). The data were corrected for Lorentz and polarization effects. The absorption corrections were based on a Gaussian grid method (SHELX76).[7] The three structures were solved by Patterson methods (SHELXS86).[8] All non-hydrogen atoms were refined (SHELXL93)[9] with anisotropic thermal parameters. All hydrogen atom coordinates were calculated with bond distances of 0.95 Å. Crystallographic data and final *R* indicies are given in Table 1. Complete crystallographic results are given in the supplemental material. For all three structures, three check reflections were measured every 3 h and showed no significant intensity loss.

Discussion

Synthesis. Divalent chalcogenolates of Yb can be prepared *via* a number of synthetic routes. All three chalcogenolates can be prepared by reacting the corresponding diphenyl dichalcogenide with the solvated metal ion in liquid ammonia. The reactions proceed through a series of color changes before the final products precipitate. The final products are relatively insoluble and must be extracted with pyridine over long periods of time; upon addition of pyridine to the final product, ammonia is slowly released over a period of days, and the resultant pyridine solutions can be filtered and the filtrates saturated with ether to give the divalent products (pyridine)$_4$Yb(SC$_6$H$_5$)$_2$ (**1**), (pyridine)$_4$Yb(SeC$_6$H$_5$)$_2$ (**2**), and (pyridine)$_5$Yb(TeC$_6$H$_5$)$_2$ (**3**). Elemental analysis indicates that these compounds lose pyridine at room temperature, with **1** and **2** desolvating over a period of weeks and **3** desolvating over a period of hours, to compounds of stoichiometry Yb(EPh)$_2$-(pyridine). Both solvent loss and the same final stoichiometry have been observed in related europium selenolate chemistry.[3d]

Alternatively, the divalent products can be prepared by reducing the dichalcogenides with a Yb/Hg amalgam. This reaction mixture gives the ytterbium dithiolate and diselenolate complexes when extracted with pyridine but does not give the corresponding tellurolate of ytterbium. Yields for **1** and **2** from the amalgam reaction are comparable to the yields obtained in the liquid ammonia reactions, and the amalgam reaction is far more convenient.

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Table 1. Crystallographic Data

	1	2	3
empirical formula	$C_{32}H_{30}N_4S_2Yb$	$C_{32}H_{30}N_2Se_2Yb$	$C_{37}H_{35}N_5Te_2Yb$
space group	$P\bar{1}$	$C2/c$	$Pbca$
a (Å)	8.797(3)	25.670(6)	13.695(9)
b (Å)	9.412(4)	9.027(4)	16.422(8)
c (Å)	9.947(7)	17.680(3)	31.917(7)
α (deg)	87.07(4)		
β (deg)	66.79(4)	133.62(2)	
γ (deg)	75.25(3)		
V (Å^3)	730.9(7)	2966(2)	7178(6)
Z	1	4	8
calcd density (g/cm^3)	1.608	1.795	1.83
no. of reflns collected	2173	4594	7305
no. of indep reflns	1983	3969	5724
no. of obsd reflns	1939 [$F > 4\sigma(F)$]	3421 [$F > 4\sigma(F)$]	3988 [$F > 4\sigma(F)$]
R indices (obsd data)[a]	$R(F) = 0.057$ $R_w(F^2) = 0.137$	$R(F) = 0.038$ $R_w(F^2) = 0.086$	$R(F) = 0.048$ $R_w(F^2) = 0.085$

[a] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w(F^2) = \{\sum[w(F_o^2 - F_c^2)^2]/\sum wF_o^4\}^{1/2}$.

By using both divalent and trivalent starting materials, we can define the limits at which ligand electronegativity is insufficient to stabilize the higher oxidation state of ytterbium. We have previously shown that the phenylselenolato anion is capable of functioning as the only anionic ligand in a Yb(III) coordination complex. In contrast, we note here that the trisphenyltellurolato complex of Yb(III) decomposes in pyridine at room temperature to give diphenyl ditelluride and **3**. The relative stability of these complexes parallels the known stability of the solid-state chalcogenides. While Yb_2Se_3 is moderately stable with respect to formation of YbSe and evaporation of Se, the analogous telluride Yb_2Te_3 was considered thermally unstable for a number of years.[10]

There is still evidence to suggest that phenyltellurolate ligand may still be able to serve as the only anionic ligand in a trivalent ytterbium complex, perhaps as some form of bimetallic chalcogenolate. After the product of the original metathesis reaction between $YbCl_3$ and 3 equiv of NaTePh in THF is taken to dryness and washed with diethyl ether, there is no evidence for the formation of PhTeTePh, and it seems unlikely that coordinated diphenyl ditelluride would not be displaced by the original THF solvent. Only after the addition and removal of pyridine from the system can PhTeTePh be isolated by extraction of the reaction mixture with diethyl ether. Further, addition of 4 equiv of NaTePh to a solution of $YbCl_3$ in THF gives an as yet unidentified ytterbium product that does not eliminate PhTeTePh upon exposure to pyridine.

Characterization. Our primary interest in these compounds was to establish whether the bonding between the ytterbium ion and the more electropositive chalcogenolate ligands should be described in purely ionic terms or whether some degree of covalent bonding contributes to complex stability. Bonds between the rare earth elements and ligands are usually described in terms of the summation of ionic radii,[11] and we set out to determine whether the Yb–E bond lengths could also be described in ionic radius summation terms. Crystals of all three divalent reaction products were characterized by low-temperature single-crystal X-ray diffraction methods, and ORTEP[12] diagrams for **1–3**, are given in Figures 1–3, respectively. Table 1 gives a crystallographic summary for all three compounds. Tables 2–4 give listings of positional parameters for **1–3**, respectively, and Tables 5–7 give listings of significant bond geometries within **1–3**, respectively.

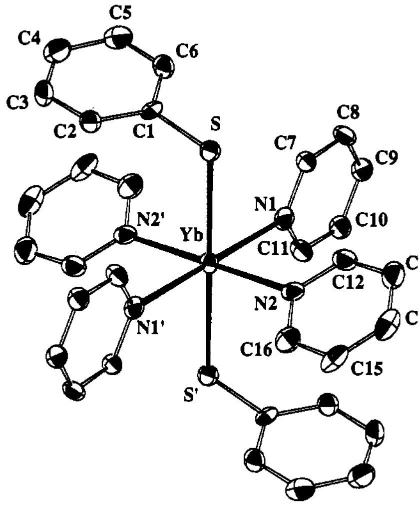

Figure 1. Molecular structure of $(pyridine)_4Yb(SC_6H_5)_2$. The octahedral Yb(II) ion is bound to *trans* phenylthiolato ligands. Significant distances (Å): Yb–S, 2.827(3); Yb–N(1), 2.565(7); Yb–N(2), 2.529(7). Significant angles (deg): S–Yb–S, 180; Yb-S-C(1), 101.6(3); N–Yb–N (*cis*), 87.1(2) and 92.9(2); N–Yb–N (*trans*), 180.0; N–Yb–S range 83.9(2)–96.1(2), average 90.

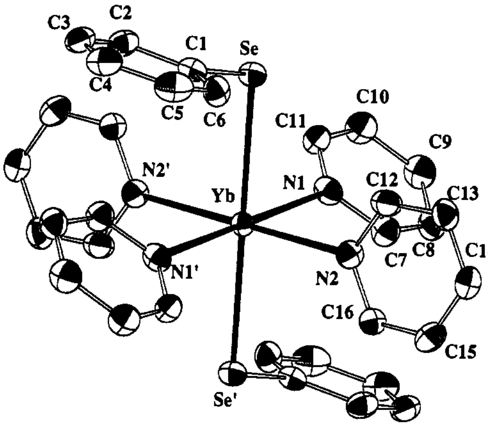

Figure 2. Molecular structure of $(pyridine)_4Yb(SeC_6H_5)_2$. The octahedral Yb(II) ion is bound to *trans* phenylselenolato ligands. Significant distances (Å): Yb–Se, 2.960(1); Yb–N(1), 2.502(4); Yb–N(2), 2.563(5); Se–C(1), 1.901(5). Significant angles (deg): Se–Yb–Se, 180; Yb–Se–C(1), 103.7(2); N(1)–Yb–N(2), 92.5(2); N–Yb–Se average 90(2).

Both **1** and **2** crystallize as regular octahedral complexes with *trans* chalcogenolate ligands. The tellurolate complex, which has the largest coordinating chalcogenide atom, coordinates a fifth pyridine ligand to form the pentagonal bipyramidal complex $(pyridine)_5Yb^{II}(TeC_6H_5)_2$ having *trans* phenyltellurolato ligands (Te–Yb–Te = 175.5(1)°) and the five pyridines around the molecular equator. The coordination of five pyridine ligands in **3** and four pyridine ligands in both **1** and **2** can be explained in

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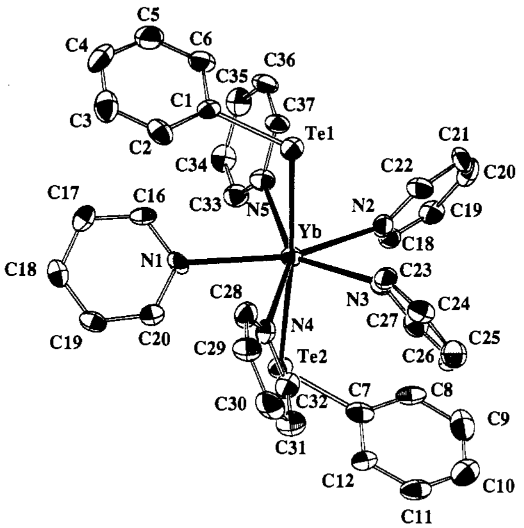

Figure 3. Molecular structure of $(pyridine)_5Yb(TeC_6H_5)_2$. The 7-coordinate Yb(II) ion contains *trans* phenyltellurolato ligands separated by a ring of 5-coordinated pyridine ligands in a pentagonal bipyramidal geometry. Average distances (Å): Yb–Te, 3.28(3); Yb–N, 2.62(1). Average angles (deg): $N\text{-}Yb\text{-}N_{adjacent}$ (i.e. N(1)–Yb–N(5)), 73(3); N–Yb–Te range 79.6–103.6°; Te–Yb–Te, 175.6(1); Yb–Te–C, 103.6(5)°.

Table 2. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å² × 10³) for **1**[a]

	x	*y*	*z*	*U*(eq)[a]
Yb	0	0	0	20(1)
S	3277(3)	534(2)	−1372(2)	24(1)
N(1)	696(11)	−889(8)	2223(7)	25(2)
N(2)	916(10)	−2674(8)	−887(7)	24(2)
C(1)	4531(12)	−1201(9)	−2275(9)	23(2)
C(2)	4511(13)	−1634(10)	−3587(9)	28(2)
C(3)	5401(14)	−3012(12)	−4267(10)	37(3)
C(4)	6397(14)	−3985(11)	−3682(12)	37(3)
C(5)	6481(14)	−3545(11)	−2405(11)	34(2)
C(6)	5575(13)	−2182(10)	−1735(9)	27(2)
C(7)	2186(13)	−882(9)	2289(9)	22(2)
C(8)	2626(13)	−1402(10)	3433(10)	26(2)
C(9)	1468(13)	−1954(9)	4583(9)	25(2)
C(10)	−47(14)	−1976(9)	4539(10)	26(2)
C(11)	−407(14)	−1446(9)	3357(10)	26(2)
C(12)	251(14)	−3176(11)	−1700(10)	29(2)
C(13)	772(15)	−4612(11)	−2260(11)	35(3)
C(14)	2005(15)	−5589(10)	−1952(10)	36(3)
C(15)	2727(14)	−5109(10)	−1117(10)	35(3)
C(16)	2128(14)	−3635(11)	−597(10)	33(3)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

terms of steric effects within the secondary coordination sphere. The Yb–E–C angles range from 101.6(3)° (E = S) to 103.7°(2) (E = Se) to 103.6(5)° (E = Te), and this phenyl group orientation puts a spatial limitation on the orientation of the pyridine ligands with respect to the N_xYb plane. Lengthening the Yb–E bond by 0.28 Å in the tellurolate complex effectively reduces the repulsions between the phenyl group on the tellurolate ligand and the pyridines, and this permits coordination of an additional ligand. This additional ligand coordination results in less than ideal orientations of the nitrogen lone pairs with respect to the metal center. In an optimum Yb–N bond, the metal would be found on the plane defined by the pyridine ring. In **1** and **2**, the average distances of the Yb atom to the planes defined by each of the four pyridine rings are 0.10 and 0.15 Å, respectively, while in **3**, the Yb distances to the individual planes defined by the pyridine ligands range from 0.03 to 0.99 Å and average 0.49 Å. Clearly in **3** the pyridine ligands are distorting from the ideal geometry to accommodate the fifth ligand.

Table 3. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å² × 10³) for **2**[a]

	x	*y*	*z*	*U*(eq)[a]
Yb	2500	2500	0	20(1)
Se	3198(1)	−381(1)	1017(1)	27(1)
N(1)	2096(2)	2411(6)	944(3)	28(1)
N(2)	1373(2)	1137(5)	−1592(3)	28(1)
C(1)	3656(3)	−872(6)	546(4)	25(1)
C(2)	3343(3)	−1879(6)	−278(4)	31(1)
C(3)	3681(3)	−2232(6)	−613(5)	35(1)
C(4)	4344(3)	−1617(7)	−138(5)	37(1)
C(5)	4668(3)	−633(7)	696(5)	39(1)
C(6)	4327(3)	−268(7)	1024(4)	31(1)
C(7)	2197(3)	3614(6)	1478(4)	31(1)
C(8)	1920(3)	3781(7)	1917(4)	33(1)
C(9)	1521(3)	2646(7)	1819(5)	36(1)
C(10)	1416(3)	1375(7)	1282(5)	35(1)
C(11)	1703(3)	1312(6)	852(4)	30(1)
C(12)	833(3)	1900(7)	−2450(4)	34(1)
C(13)	205(3)	1251(7)	−3345(4)	34(1)
C(14)	120(3)	−258(7)	−3366(4)	31(1)
C(15)	673(3)	−1068(7)	−2476(5)	32(1)
C(16)	1285(3)	−349(6)	−1616(4)	26(1)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

The ytterbium(II)–chalcogen bond lengths can be described in simple ionic radius summation terms.[11] If we first quantify the effect of changing the metal coordination number by comparing metal–nitrogen distances (the average Yb–N distance in 7-coordinate **4** (2.62(1)Å) is slightly longer, by 0.08 Å, than the average Yb–N distance (2.54(2)Å) in octahedral **1** or **2**) and then consider the difference in chalcogenide size (0.23 Å), we would predict the Yb–Te bond length to be 0.31 Å longer than the Yb–Se bond length. The actual change in Yb–chalcogen distance upon substituting Te for Se, 0.32 Å, is consistent with the purely ionic bonding description. Because the S and Se derivatives have identical coordination numbers, a bond length comparison is more straightforward. Shannon[11] predicts an increase in bond length of 0.14 Å upon substitution of S by Se, and the observed bond length change, 0.134 Å.

The predicted differences between Yb(II) and Yb(III) chalcogenolates are not as accurately predicted by ionic radii. Shannon's tables list a difference between Yb(II) and Yb(III) ionic radii of 0.15 Å (for coordination number 6). If we compare the Yb–N and Yb–Se distances in **2** with the Yb–N and terminal Yb–Se distances in $YbLi(SePh)_4(pyridine)_4$,[3c] we see that there are significant deviations from ideal bond length behavior; the Yb–N bond lengths differ by 0.10 Å, while the Yb–Se bond lengths differ by 0.19 Å.

It is difficult to obtain useful information about solution structure from NMR experiments, because overlap with pyridine resonances preclude NMR analysis in deuterated pyridine. Attempts at NMR analysis in THF or CD_3CN tend to result in the formation of a precipitate within minutes, presumably due to the formation of coordination polymers. These precipitates can be redissolved in pyridine to give the original molecular complex.

In pyridine solution the UV–visible spectra of all three complexes are concentration dependent. All three complexes show a pair of intense absorptions, with the higher energy excitation having a narrower line width. By analogy with the pyridine and THF coordination complexes of $Eu(SePh)_2$,[3d] we tentatively assign the lowest energy UV–visible absorptions of the divalent complexes **1**–**3** to some form of a metal to pyridine charge-transfer excitation. At ca. 10^{-3} M concentrations the visible spectrum of **1** shows absorption bands at λ_{max} = 302 and 577 nm. Compound **2** has absorptions at λ_{max} = 307 and 552 nm, and **3** has absorptions at λ_{max} = 391 and 525 nm. In all three spectra, the two absorptions have similar cross sections at the low-concentration limit, while at higher concentrations (>10^{-2} M) the relative intensity of the low-energy band decreases and the higher energy band shifts to lower energy. At ca. 10^{-3} M

Table 4. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **3**[a]

	x	*y*	*z*	*U*(eq)[a]
Yb	299(1)	7311(1)	1261(1)	23(1)
Te(1)	300(1)	6910(1)	2257(1)	29(1)
Te(2)	275(1)	7567(1)	230(1)	30(1)
C(1)	−632(7)	5875(5)	2315(3)	24(2)
C(2)	−267(9)	5097(5)	2236(3)	34(2)
C(3)	−878(10)	4426(6)	2271(3)	44(3)
C(4)	−1852(9)	4530(7)	2390(3)	45(3)
C(5)	−2193(10)	5303(7)	2460(3)	46(3)
C(6)	−1606(8)	5961(6)	2428(3)	35(3)
C(7)	1258(8)	8553(6)	140(3)	31(2)
C(8)	955(8)	9363(6)	187(3)	32(2)
C(9)	1603(10)	9996(6)	125(3)	45(3)
C(10)	2556(10)	9851(7)	19(3)	43(3)
C(11)	2850(8)	9065(7)	−33(3)	38(3)
C(12)	2228(7)	8430(6)	31(3)	30(2)
N(1)	−223(6)	5843(4)	1040(2)	28(2)
C(13)	198(7)	5489(5)	708(3)	25(2)
C(14)	−43(7)	4722(6)	572(3)	29(2)
C(15)	−757(8)	4289(5)	778(3)	29(2)
C(16)	−907(8)	5405(6)	1242(3)	29(2)
C(17)	−1187(7)	4632(5)	1133(3)	29(2)
N(2)	−340(6)	8803(4)	1310(2)	30(2)
C(18)	−888(8)	9156(5)	1011(3)	29(2)
C(19)	−1388(8)	9878(6)	1069(3)	31(2)
C(20)	−1332(8)	10247(6)	1453(3)	36(3)
C(21)	−770(8)	9895(5)	1760(3)	32(2)
C(22)	−272(8)	9186(5)	1676(3)	32(2)
N(3)	1776(6)	8193(4)	1504(2)	28(2)
C(23)	2474(8)	7971(6)	1788(3)	34(2)
C(24)	3398(7)	8268(6)	1790(3)	33(2)
C(25)	3674(9)	8812(7)	1486(3)	47(3)
C(26)	2998(8)	9056(6)	1202(3)	42(3)
C(27)	2074(8)	8740(6)	1221(3)	35(3)
N(4)	1980(6)	6562(4)	1147(2)	26(2)
C(28)	2367(8)	6062(6)	1436(3)	36(3)
C(29)	3322(8)	5844(6)	1442(3)	35(3)
C(30)	3946(9)	6161(6)	1138(3)	45(3)
C(31)	3578(8)	6681(6)	843(3)	39(3)
C(32)	2604(8)	6856(6)	858(3)	33(3)
N(5)	−1616(6)	7318(5)	1316(2)	28(2)
C(33)	−2183(8)	7201(5)	982(3)	32(2)
C(34)	−3192(8)	7257(6)	984(3)	32(2)
C(35)	−3649(8)	7445(6)	1348(3)	37(3)
C(36)	−3089(8)	7553(5)	1704(3)	35(3)
C(37)	−2086(8)	7504(5)	1674(3)	27(2)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for **1**[a]

Yb–N(2)′	2.529(7)	S–C(1)	1.772(9)
Yb–N(2)	2.529(7)	N(1)–C(7)	1.34(1)
Yb–N(1)′	2.565(7)	N(1)–C(11)	1.35(1)
Yb–N(1)	2.565(7)	N(2)–C(12)	1.33(1)
Yb–S	2.827(3)	N(2)–C(16)	1.33(1)
Yb–S′	2.827(3)		
N(2)′–Yb–N(2)	180.0	N(1)′–Yb–S	90.7(2)
N(2)′–Yb–N(1)′	87.1(2)	N(1)–Yb–S	89.3(2)
N(2)–Yb–N(1)′	92.9(2)	N(2)′–Yb–S′	96.1(2)
N(2)′–Yb–N(1)	92.9(2)	N(2)–Yb–S′	83.9(2)
N(2)–Yb–N(1)	87.1(2)	N(1)′–Yb–S′	89.3(2)
N(1)′–Yb–N(1)	180.0	N(1)–Yb–S′	90.7(2)
N(2)′–Yb–S	83.9(2)	S–Yb–S′	180.0
N(2)–Yb–S	96.1(2)	C(1)–S–Yb	101.6(3)

[a] Symmetry transformation used to generate equivalent atoms: (prime) $-x, -y, -z$.

Table 6. Selected Bond Lengths (Å) and Angles (deg) for **2**[a]

Yb–N(1)	2.502(4)	N(1)–C(7)	1.341(7)
Yb–N(2)	2.563(5)	N(1)–C(11)	1.342(7)
Yb–Se	2.960(1)	N(2)–C(12)	1.340(7)
Se–C(1)	1.901(5)	N(2)–C(16)	1.356(7)
N(1)–Yb–N(2)	92.5(2)	N(2)–Yb–Se	89.8(1)
N(1)–Yb–N(2)′	87.5(2)	N(2)′–Yb–Se	90.2(1)
N(1)′–Yb–Se	94.4(1)	C(1)–Se–Yb	103.7(2)
N(1)–Yb–Se	85.6(1)		

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

Table 7. Selected Bond Lengths (Å) and Angles (deg) for **3**

Yb–N(3)	2.607(8)	Yb–Te(1)	3.248(1)
Yb–N(2)	2.608(7)	Yb–Te(2)	3.315(1)
Yb–N(1)	2.611(7)	Te(1)–C(1)	2.133(9)
Yb–N(5)	2.629(8)	Te(2)–C(7)	2.125(10)
Yb–N(4)	2.635(8)		
N(3)–Yb–N(2)	73.7(3)	N(1)–Yb–Te(1)	94.4(2)
N(3)–Yb–N(1)	143.7(2)	N(5)–Yb–Te(1)	86.3(2)
N(2)–Yb–N(1)	142.4(3)	N(4)–Yb–Te(1)	92.3(2)
N(3)–Yb–N(5)	138.7(2)	N(3)–Yb–Te(2)	103.4(2)
N(2)–Yb–N(5)	69.9(2)	N(2)–Yb–Te(2)	86.4(2)
N(1)–Yb–N(5)	75.5(2)	N(1)–Yb–Te(2)	81.2(2)
N(3)–Yb–N(4)	67.8(2)	N(5)–Yb–Te(2)	93.3(2)
N(2)–Yb–N(4)	137.8(2)	N(4)–Yb–Te(2)	86.0(2)
N(1)–Yb–N(4)	76.8(2)	Te(1)–Yb–Te(2)	175.58(2)
N(5)–Yb–N(4)	152.0(2)	C(1)–Te(1)–Yb	104.2(2)
N(3)–Yb–Te(1)	79.7(2)	C(7)–Te(2)–Yb	103.0(2)
N(2)–Yb–Te(1)	97.6(2)		

concentrations, the molar absorptivity values are roughly 6×10^4 M^{-1} cm^{-1} for the higher energy bands and 3×10^4 M^{-1} cm^{-1} for the lower energy bands, but these values must be considered approximations, due to the thermal instability of the isolated crystalline compounds. We tentatively attribute these concentration-dependent visible absorptions to an equilibrium between monomeric and oligiomeric species with chalcogenolate ligands bridging metal centers (a phenylchalcogenolate disproportionation reaction to form a cation/anion pair is another possible process). The inverse relationship between increasing chalcogenolate electronegativity and decreasing absorption energy can then be interpreted in terms of increasingly electronegative chalcogenolate ligands preferentially stabilizing the higher Yb(III) oxidation state. The increase in excitation energy upon substituting S with Se or Se with Te is similar in magnitude to the difference in absorption energy between the selenolate[3d] and tellurolate[3e] of Eu(II).

Conclusion

The divalent ytterbium chalcogenolates $Yb(EPh)_2$ (E = S, Se, Te) can be isolated as crystalline pyridine coordination complexes. The stability of rare earth metal chalcogenolate complexes is dependent on the steric/electronic properties of the chalcogenolate ligand and the identity of the donor ligands bound to the metal; trivalent selenolate complexes are known to be stable in both pyridine and THF, whereas the trivalent tellurolate complex of ytterbium reductively eliminates diphenyl ditelluride to form a Yb(II) complex in pyridine. Pyridine readily solubilizes divalent ytterbium thiolato, selenolato, and tellurolato complexes, and when isolated, these complexes are thermally unstable with respect to pyridine dissociation at room temperature. Structural characterization of all three divalent complexes show that the Yb–chalcogen bond length can be predicted from ionic radius summation rules. The lowest energy transitions in the UV–visible spectra of these complexes are interpreted in terms of a metal to pyridine charge-transfer excitation, with the more electronegative ligands preferentially stabilizing the trivalent oxidation state.

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Supplementary Material Available: Tables of crystallographic details, bond lengths, bond angles, anisotropic displacement parameters, hydrogen coordinates and isotropic displacement parameters, torsion angles, and least-squares planes for **1**–**3** (28 pages). Ordering information is given on any current masthead page.