Early- and Late-Lanthanide Pyridinethiolates: Synthesis, Redox Stability, and Structure

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The early and late lanthanides form stable complexes with the pyridinethiolate (2-S-NC_5H_4, or SPy) ligands. The Ce compound $Ce(SPy)_3$ is relatively insoluble in neutral organic donor solvents such as THF or pyridine but can be solubilized by the addition of $[PEt_4][SPy]$ to form the orange homoleptic cerium thiolate $[PEt_4][Ce(SPy)_4]$ (**1**). Low-temperature structural characterization of **1** showed that the complex is isostructural with the known Eu(III) derivative. Further oxidation of Ce(III) with dipyridyl disulfide does not occur. Molecular **1** is colored due to a low-energy f^1-to-d^1 promotion. As the size of the lanthanide ion decreases, the solubility of neutral $Ln(SPy)_3$ appears to increase. Colorless $[PEt_4][Ln(SPy)_4]$ (Ln = Ho (**2**), Tm (**3**)) can also be isolated by fractional crystallization, and the compounds are isostructural with the Ce and Eu derivatives. The neutral complexes of Ho and Tm are also slightly soluble in acetonitrile and dimethoxyethane and very soluble in pyridine. Both divalent and trivalent Yb complexes of the pyridinethiolate ligand dissolve in and crystallize from pyridine. Divalent $Yb(SPy)_2$ crystallizes as the pentagonal bipyramidal molecule $(py)_3Yb(SPy)_2$ (**4**). One pyridine nitrogen and the four donor atoms of the two pyridinethiolate ligands are bound in equatorial positions, and two neutral pyridine ligands occupy the axial sites. The Yb(III) compound crystallizes readily from pyridine as molecular 8-coordinate $(py)_2Yb(SPy)_3$ (**5**). Compounds **4** and **5** are intensely colored; **4** has a visible Yb(II)-to-pyridine charge transfer excitation that is virtually identical in energy to the analogous excitation in $SmI_2(py)_4$, while **5** has a visible S-to-Yb charge transfer absorption. Crystal data (Mo Kα, 153(5) K) are as follows: **1**, monoclinic space group $P2/n$, $a = 15.118(6)$ Å, $b = 16.117(4)$ Å, $c = 26.443(7)$ Å, $\beta = 90.14(3)°$, $Z = 4$; **4**, monoclinic space group Cc, $a = 10.588(1)$ Å, $b = 16.810(3)$ Å, $c = 14.833(5)$ Å, $\beta = 109.12(2)°$, $Z = 4$; **5**, monoclinic space group $P2_1/n$, $a = 9.672(2)$ Å, $b = 16.293(4)$ Å, $c = 19.214(3)$ Å, $\beta = 101.51(2)°$, $Z = 4$.

Introduction

The pyridinethiolate ligand (2-S-NC_5H_4, or SPy) has been applied extensively[1] to the synthesis of main group and transition metal compounds and has been particularly useful for the synthesis of compounds in what would otherwise be unobtainable oxidation states for a homoleptic thiolate (i.e., Rh(III)[1f] or Pt(III)[1a]). The recent description of a stable Eu(III) pyridinethiolate compound[2] supports the contention that this resonance-stabilized ligand is particularly suited to stabilizing higher oxidation states, since Eu(III) arenethiolates were recently described as unstable with respect to the formation of disulfides and Eu(II) thiolates.[3]

An investigation of pyridinethiolate chemistry of the early and late redox-active lanthanides is merited for a number of reasons. First, $Ln(SPy)_x$ complexes are interesting from a structural perspective. With few exceptions,[4] the chemistry of the Ln elements can be described entirely by ionic bonding models in which oxidation state and coordination number are the only important factors that influence M−L bond lengths. Ionic bonding models will predict that, for a given coordination complex, all cation−anion bond lengths should be equivalent if the coordination numbers are identical, and yet there are descriptions of octahedral $Yb(SR)_3$ coordination complexes in the literature that contain inequivalent Ln−S bonds.[5] Structural characterization of additional Ln(III) thiolate derivatives will be helpful in establishing the origins of the inequivalent Yb−S bond lengths. Second, divalent lanthanides are often used as one-electron-reducing agents in organic synthesis,[6] and the unusual hard/soft donor capacity of the pyridinethiolate ligands

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can have a measurable influence on redox stability, possibly to the extent that novel reducing agents with superior chemical or physical properties can be prepared. Third, in Ce chemistry, the recent description of Ce(COT)$_2$ as a Ce(III) compound[7] is a reminder that Ce(IV) compounds are attractive synthetic targets. Thiolates of cerium may also be useful in developing Ce$_2$S$_3$ pigments[8] as an alternative to the more toxic group 12 sulfides. For these reasons we have investigated the redox and structural chemistry of the early (Ce) and late (Yb) Ln elements with the SPy ligand.

Experimental Section

General Methods. All syntheses were carried out under ultrapure nitrogen (JWS), using conventional drybox or Schlenk techniques. THF and pyridine (Fisher) were refluxed continuously over K and KOH, respectively, and collected immediately prior to use. Dipyridyl disulfide, mercaptopyridine, Et$_4$PCl, and NaHBEt$_3$ were purchased from Aldrich. Ce, Tm, Ho, Yb, and Hg were purchased from Strem. 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 450 cm^{-1} as a Nujol mull. 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). NMR Spectra were obtained on either a Varian Gemini 300 MHz or a Varian 400 MHz NMR spectrometer and are reported in δ (ppm).

Synthesis of [PEt$_4$][Ce(S-2-NC$_5$H$_4$)$_4$] (1). Ce (0.96 g, 6.9 mmol), dipyridyl disulfide (3.02 g, 13.7 mmol), and Hg (0.13 g, 0.65 mmol) were stirred for 24 h at room temperature, and a white precipitate formed. In a separate reaction vessel, 2-mercaptopyridine (0.72 g, 6.5 mmol) was dissolved in THF (30 mL) and Na[Et$_3$BH] (6.5 mL of a 1.0 M solution in THF, 6.5 mmol) was added *via* syringe. The solution was stirred for 30 min, and then [Et$_4$P]Cl(1.2 g, 6.5 mmol) was added as a solid. This solution was refluxed for 10 min and then added to the Ce reaction mixture. Immediately upon mixing, the solution turned deep red. The solution was refluxed for 18 h and then filtered. The red solution was concentrated under vacuum to 40 mL and layered with ether (80 mL). After several days [PEt$_4$][Ce(S-2-NC$_5$H$_4$)$_4$] (2.0 g, 40%) was isolated as deep orange crystals. The solid appears to decompose above 160 °C but becomes an orange liquid between 200 and 205 °C with the elimination of a white solid. Anal. Calcd for C$_{28}$H$_{36}$N$_4$CePS$_4$: C, 46.2; H, 4.89; N, 7.52. Found: C, 45.8; H, 5.00; N, 7.70. ^{1}H NMR (CD$_3$CN, 20 °C): 17.02 (m, 1H), 8.97 (m, 1H), 8.37 (m, 1H), 7.70 (m, 1H), 1.58 (m, 8H), 0.82 (m, 12H). Only a single set of ^{1}H NMR resonances were detected even when the temperature of the sample was lowered to -50 °C. A plot of ^{1}H NMR chemical shift vs 1/T showed only ideal Curie$-$Weiss behavior for all four proton resonances. ^{13}C NMR (CD$_3$CN, 20 °C): 154.8, 151.1, 139.3, 132.8, 123.9, 11.3 (d), 5.4 (d). λ_{max}: 447 nm (C$_5$H$_5$N). The IR spectra of **1**$-$**3** are essentially identical to that of the Eu derivative.[2]

Synthesis of [PEt$_4$][Tm(S-2-NC$_5$H$_4$)$_4$] (2). 2-Mercaptopyridine (0.47 g, 4.0 mmol) was dissolved in THF (50 mL), and NaHBEt$_3$ (4.0 mL of a 4.0 M solution in THF, 4.0 mmol) was added *via* syringe. This solution was stirred for 30 min, and the solvent was removed under vacuum to leave a white solid. Hg (55 mg, 0.27 mmol), Tm (0.676 g, 4 mmol), 2,2′-dithiodipyridine (1.32 g, 6.0 mmol), Et$_4$PCl (0.731 g, 4 mmol), and CH$_3$CN (50 mL) were added to the white solid, and the solution was refluxed for 18 h. The bright orange solution was filtered and concentrated (20 mL). The solution was refluxed to redissolve precipitated material and then cooled (-20 °C) to give crystals of **3** (1.8 g, 60%; mp 250$-$60 °C) that were collected by filtration. Anal. Calcd for C$_{28}$H$_{36}$N$_4$TmPS$_4$: C, 44.4; H, 4.80; N, 7.40. Found: C, 43.8; H, 4.64; N, 7.50.

Synthesis of [PEt$_4$][Ho(S-2-NC$_5$H$_4$)$_4$] (3). 2-Mercaptopyridine (0.47 g, 4.0 mmol) was dissolved in THF (50 mL), and NaHBEt$_3$ (4.0 mL of a 4.0 M solution in THF, 4.0 mmol) was added *via* syringe. This solution was stirred for 30 min, and the solvent was removed under vacuum to leave a white solid. Hg (55 mg, 0.27 mmol), Ho (0.656 g, 4 mmol), 2,2′-dithiodipyridine (1.32 g, 6.0 mmol), Et$_4$PCl (0.73 g, 4.0 mmol), and CH$_3$CN (50 mL) were added to the white solid, and the solution was refluxed for 18 h. The bright orange solution was filtered while hot, and the filtrate was concentrated (20 mL) and cooled (-20 °C) to give crystals of **3** (1.93 g, 64%; mp 250$-$70 °C dec 280 °C), which were collected by filtration. The compound crystallizes initially as long colorless needles and subsequently as colorless blocks. The unit cells for both crystal habits were identical and isostructural with the Eu and Ce derivatives. Anal. Calcd for C$_{28}$H$_{36}$N$_4$HoPS$_4$: C, 44.7; H, 4.82; N, 7.44. Found: C, 44.4; H, 4.80; N, 7.34.

Synthesis of (py)$_3$Yb(S-2-C$_5$H$_4$N)$_2$ (4). Yb (0.71 g, 4.1 mmol), dipyridyl disulfide (0.84 g, 3.8 mmol), and Hg (6.6 g,33 mmol) were stirred in pyridine (50 mL). The reaction mixture quickly turned bright yellow and then deep green after 30 min. The reaction was allowed to proceed for 5 h and then refluxed to dissolve the green precipitate. The solution was filtered while hot, and the filtrate was allowed to cool to room temperature as green crystals precipitated. After 24 h, the solution was placed at -20 °C for another day before (py)$_3$Yb(S-2-C$_5$H$_4$N)$_2$ (1.2 g, 50%) was isolated. The solid loses pyridine rapidly above 100 °C and does not melt below 300 °C. The compound loses pyridine upon removal from the mother liquor and reaches a final stoichiometry of (py)$_2$Yb(S-2-C$_5$H$_4$N)$_2$. Anal. Calcd for C$_{20}$H$_{13}$N$_4$S$_2$-Yb: C, 43.9; H, 2.40; N, 10.3. Found: C, 43.5; H, 2.32; N, 10.2. The ^{1}H NMR in either C$_5$D$_5$N or CD$_3$CN show broad uninterpretable signals between -40 and 50 °C. ^{13}C NMR (C$_5$D$_5$N, 20 °C): 177.0, 144.7, 128.5, 127.5, 114.8, 113.2, 95.7, 93.5, 86.8, 86.4. λ_{max}: 494 nm (CH$_3$CN); 667 nm (C$_5$H$_5$N). IR: 2358 (m), 1916 (w), 1857 (w), 1577 (m), 1451 (s), 1374 (s), 1220 (w), 1131 (m), 1070 (w), 1020 (w), 977 (m), 729 (s), 611 (m), 530 (m) cm^{-1}.

Synthesis of (py)$_2$Yb(S-2-C$_5$H$_4$N)$_3$·py (5). Yb(2.09 g, 12.1 mmol), (S-2-C$_5$H$_4$N)$_2$ (4.0 g, 18 mmol), and Hg(S-2-C$_5$H$_4$N)$_2$ (0.10 g, 0.23 mmol) were stirred for 18 h in pyridine (70 mL) at room temperature. The bright yellow solution was filtered, and the filtrate was concentrated to 30 mL under vacuo and allowed to sit at -20 °C for 24 h. Yellow crystals of (py)$_2$Yb(S-2-C$_5$H$_4$N)$_3$·py (7.8 g, 87%) began to form upon cooling. The product loses pyridine above 100 °C and becomes noticeably opaque above 300 °C. Anal. Calcd for C$_{30}$H$_{17}$N$_6$S$_3$Yb: C, 48.6; H, 3.68; N, 11.3. Found: C, 48.2; H, 3.59; N, 11.2. ^{1}H NMR (C$_5$D$_5$N, 20 °C): -4.86 (m, 1H), -7.84 (m, 1H), -8.37 (m, 1H), -26.4 (m, 1H). λ_{max} (in pyridine): 388 nm. IR: 1653 (w), 1578 (m), 1455 (s), 1375 (s), 1261 (m), 1135 (m), 1091 (m), 1029 (m), 803 (m), 732 (m) cm^{-1}.

X-ray Structure Determination of **1**, **4**, and **5**. Data for **1** , **4**, and **5** were collected on a CAD4 diffractometer with graphite monochromatized Mo Kα radiation, $\lambda = 0.710\,73$ Å, at 153 K. The crystals were isolated, immersed (within seconds) into a 50/50 mixture of mineral and dry, degassed Paratone-N oils, and examined under a polarizing microscope. All samples were mounted on a glass fiber within minutes of isolation from the mother liquor and cooled rapidly, in order to minimize problems related to neutral ligand dissociation. In all structures, three check reflections were measured every hour and

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Table 1. Crystal Data and Structure Refinement Details for $[PEt_4][Ce(S\text{-}2\text{-}NC_5H_4)_4]$ (**1**), $(py)_3Yb(S\text{-}2\text{-}NC_5H_4)_2$ (**4**), and $(py)_2Yb(S\text{-}2\text{-}NC_5H_4)_3$ (**5**)[a]

	1	4	5
empirical formula	$C_{28}H_{36}CeN_4P_2S_4$	$C_{25}H_{23}N_5S_2Yb$	$C_{30}H_{27}N_6S_3Yb$
fw	1455.88	630.64	740.80
space group	$P2/n$	Cc	$P2_1/n$
a (Å)	15.118(6)	10.588(1)	9.672(2)
b (Å)	16.117(4)	16.810(3)	16.293(4)
c (Å)	26.443(7)	14.833(5)	19.214(3)
α (deg)	90	90	90
β (deg)	90.14(3)	109.12(2)	101.51(1)
γ (deg)	90	90	90
V (Å^3)	6443(4)	2494(1)	2967(1)
Z	8	4	4
D(calcd) (g/cm^3)	1.501	1.679	1.658
temp (°C)	−120	−120	−120
λ (Å)	0.710 73	0.710 73	0.710 73
abs coeff (mm^{-1})	1.746	3.939	3.394
no. of obsd reflcns [$I > 2\sigma(I)$]	4251	2722	4248
final $R(F)$ [$I > 2\sigma$]	0.045	0.026	0.033
$R_w(F^2)$ [$I > 2\sigma(I)$]	0.077	0.071	0.075

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

indicated an overall decay of less than 2%. The data were corrected for Lorentz effects and polarization. The absorption corrections for **1**, **4**, and **5** were based on a Gaussian grid method (SHELX76).[9] The structures were solved by direct methods (SHELXS86).[10] All non-hydrogen atoms were refined (SHELXL93)[11] on the basis of F_o^2. All hydrogen atom coordinates were calculated with idealized geometries (SHELXL93). Scattering factors (f_0, f', f'') are as described in SHELXL93. Crystallographic data and final R indices are given in Table 1. Complete crystallographic details are given in the Supporting Information.

Results and Discussion

Synthesis and Structural Characterization. Elemental Ce reacts with PySSPy in pyridine to form a precipitate that is insoluble in conventional donor solvents such as THF, acetonitrile, or pyridine. The reaction product can be solubilized by addition of further pyridinethiolate anion and crystallized from either pyridine or acetonitrile as the phosphonium salt $[PEt_4][Ce(SPy)_4]$ (**1**) (eq 1). The orange crystals were characterized

$$\mathrm{Ce} + {}^{3}/_{2}\mathrm{PySSPy} \xrightarrow{\text{pyridine}} \text{insoluble } \mathrm{Ce(SPy)_3} \xrightarrow{\mathrm{PEt_4SPy}} [\mathrm{PEt_4}][\mathrm{Ce(SPy)_4}] \quad (1)$$

by low temperature single-crystal X-ray diffraction and shown to be isostructural with the recently reported Eu(III) derivative.[2] In **1**, as in the Eu complex, the structure contains three different 8-coordinate Ln(III) ions in the unit cell (see Figure 1). There are no significant differences between the bond geometries of the Ce (see Table 2) and Eu complexes. The observation of three distinct coordination geometries in a single-crystalline lattice indicates that crystal packing forces have a significant impact on observed solid state structure. Similar behavior has been noted in the structural chemistry of the $Ce(S_2PMe_2)_4^-$ ion, which crystallizes as both a square antiprism and a dodecahedron within the same unit cell,[12] and in the Ph_4As^+ [13] and Ph_4P^+ [14] salts of the $Pr(S_2PMe_2)_4^-$ anion, which are not isomorphous.

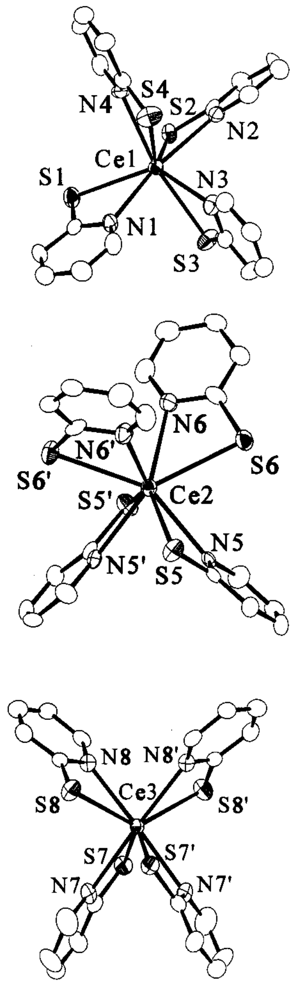

Figure 1. Molecular structure of the three inequivalent anions in the unit cell of $[PEt_4][Ce(S\text{-}2\text{-}NC_5H_4)_4]$ (**1**).

Stable Ce(IV) compounds are often targeted synthetically because of their relative scarcity and their utility as oxidizing agents. Homoleptic cerium(IV) alkoxides are stable, and there is considerable discussion in the literature as to whether $Ce(C_8H_8)_2$ contains a Ce(III) or a Ce(IV) ion.[4] Still, the pyridinethiolate ligand does not appear sufficiently electronegative to stabilize Ce(IV). There is no apparent reaction of **1** with excess dipyridyl disulfide, and both **1** and dipyridyl disulfide can be isolated from metathesis reactions using Ce(IV) starting materials. Reductive elimination of REER has considerable precedence as a decomposition pathway in redox-active $Ln(ER)_x$ chemistry,[15] and the stability of cerium(IV) isopropoxide[16] but not cerium(IV) pyridinethiolate can be attributed to the strength of the S−S bonds (66 kcal/mol in HSSH[17]) relative to the weaker O−O bonds (51(1) kcal/mol in HOOH[17]) that would be produced in reductive elimination processes.

The 8-coordinate structure of **1** can be reproduced through most of the lanthanide series. Colorless derivatives of Tm (**2**) and Ho (**3**) have been prepared in order to address questions related to electronic structure and thermolysis chemistry, and

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Table 2. Significant Bond Lengths (Å) and Angles (deg) for the Anions in **1**[a]

Ce(1)−N(2)	2.564(7)	Ce(1)−N(4)	2.606(7)
Ce(1)−S(1)	2.912(3)	Ce(1)−S(4)	2.928(3)
S(1)−C(1)	1.740(9)	S(3)−C(11)	1.729(10)
Ce(2)−N(5)′	2.588(7)	Ce(2)−N(6)	2.606(7)
Ce(2)−S(5)	2.924(3)	Ce(2)−S(6)	2.935(3)
S(5)−C(21)	1.748(9)	Ce(3)−N(7)″	2.597(8)
Ce(3)−N(8)	2.606(7)	Ce(3)−S(8)	2.907(3)
Ce(3)−S(7)	2.961(3)	S(7)−C(31)	1.737(9)
N(2)−Ce(1)−N(3)	86.0(2)	N(3)−Ce(1)−N(4)	131.9(2)
N(3)−Ce(1)−N(1)	76.5(2)	N(2)−Ce(1)−S(1)	142.6(2)
N(4)−Ce(1)−S(1)	85.5(2)	N(2)−Ce(1)−S(3)	90.3(2)
N(4)−Ce(1)−S(3)	162.0(2)	S(1)−Ce(1)−S(3)	99.68(8)
N(2)−Ce(1)−S(4)	85.2(2)	N(3)−Ce(1)−S(4)	78.7(2)
N(1)−Ce(1)−S(4)	83.3(2)	S(3)−Ce(1)−S(4)	135.06(8)
N(3)−Ce(1)−S(2)	126.9(2)	N(1)−Ce(1)−S(2)	142.1(2)
S(3)−Ce(1)−S(2)	85.08(8)	N(5)′−Ce(2)−N(5)	77.2(3)
N(5)−Ce(2)−N(6)	121.0(2)	N(5)−Ce(2)−N(6)′	131.1(2)
N(6)−Ce(2)−S(5)	142.2(2)	N(5)′−Ce(2)−S(5)′	57.2(2)
N(6)−Ce(2)−S(5)′	77.7(2)	S(5)−Ce(2)−S(5)′	134.73(11)
N(5)′−Ce(2)−S(6)	149.4(2)	N(5)−Ce(2)−S(6)	75.9(2)
N(6)′−Ce(2)−S(6)	88.0(2)	S(5)′−Ce(2)−S(6)	106.68(7)
N(5)−Ce(2)−S(6)′	149.4(2)	S(5)′−Ce(2)−S(6)′	90.96(7)
N(7)″−Ce(3)−N(7)	74.8(3)	N(7)−Ce(3)−N(8)	101.7(2)
N(7)−Ce(3)−N(8)″	173.7(2)	N(7)″−Ce(3)−S(8)	127.9(2)
N(7)″−Ce(3)−S(8)″	90.1(2)	N(8)−Ce(3)−S(8)″	87.9(2)
S(8)−Ce(3)−S(8)″	134.29(11)	N(7)″−Ce(3)−S(7)	85.7(2)
N(8)″−Ce(3)−S(7)	130.3(2)	S(8)″−Ce(3)−S(7)	74.45(7)
N(7)−Ce(3)−S(7)″	85.7(2)	N(8)″−Ce(3)−S(7)″	88.0(2)
S(8)″−Ce(3)−S(7)″	125.72(7)		

[a] Symmetry transformations used to generate equivalent atoms: (′) $-x + {}^1/_2, y, -z + {}^1/_2$. (″) $-x + {}^3/_2, y, -z + {}^1/_2$.

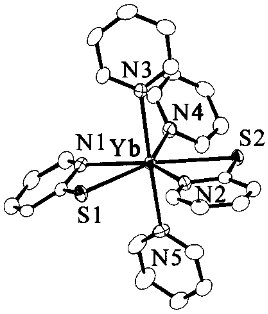

Figure 2. Molecular structure of $(py)_3Yb(S\text{-}2\text{-}NC_5H_4)_2$ (**4**).

the unit cell of the Tm compound indicates that the compound is isostructural with the Eu and Ce compounds. While the physical properties of **2** and **3** are similar to those of the early-Ln ions, the solubilities of the neutral $Ln(SPy)_3$ compounds are not. Both $Ce(SPy)_3$ and $Eu(SPy)_3$ are insoluble in THF, acetonitrile, and pyridine, while in the later half of the lanthanide series the neutral complexes become considerably more soluble as the size of the metal decreases, to the extent that crystalline $Ln(SPy)_3$ coordination complexes can be isolated from pyridine.

Crystalline pyridinethiolate derivatives of Yb(II) and Yb(III) can be prepared by reduction of the disulfide with elemental Yb in pyridine (eq 2) and isolated as the pyridine coordination

$$\mathrm{Yb} + \mathrm{PySSPy} \xrightarrow{\text{pyridine}} (\mathrm{py})_3\mathrm{Yb(SPy)}_2 \xrightarrow{{}^1/_2\mathrm{PySSPy}} (\mathrm{py})_2\mathrm{Yb(SPy)}_3 \quad (2)$$

complexes $(py)_3Yb(SPy)_2$ (**4**) (see Figure 2) and $(py)_2Yb(SPy)_3$ (**5**) (see Figure 3). Tables 3 and 4 give a listing of significant bond lengths and angles for compounds **4** and **5**, respectively. Divalent **4** contains a pentagonal bipyramidal Yb(II) ion with the four donor atoms of the two pyridinethiolate ligands and a neutral pyridine in the equatorial positions and two pyridine ligands in the axial sites (N−Yb−N = 170°). The difference in coordination number between **4** and octahedral $(py)_4Yb(SPh)_2$[18] is attributable to the smaller steric requirements of the chelating ligand relative to two monodentate ligands. The Yb−S distances in **4** are statistically inequivalent (Yb−S(1) = 2.839(2) Å; Yb−S(2) = 2.929(2) Å), and the chemical similarity of the coordination sites indicates that these divalent Yb−S bonds are easily distorted. The Yb−S bonds in 7-coordinate **4** are within 0.03 Å of the Yb−S bond lengths that would be predicted from the structure of $(py)_4Yb(SPh)_2$ ($Yb{-}S_{av}$ = 2.827(3) Å) when adjustment for the difference in coordination number is considered.[19]

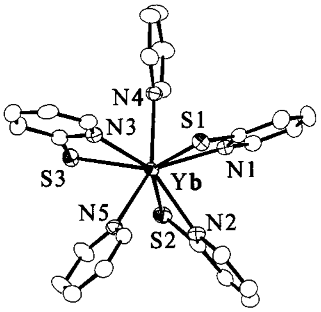

Figure 3. Molecular structure of $(py)_2Yb(S\text{-}2\text{-}NC_5H_4)_3$ (**5**).

Table 3. Significant Bond Lengths (Å) and Angles (deg) for **4**

Yb−N(2)	2.524(5)	Yb−N(3)	2.533(5)
Yb−N(1)	2.560(5)	Yb−N(5)	2.568(5)
Yb−N(4)	2.582(5)	Yb−S(1)	2.839(2)
Yb−S(2)	2.929(2)	S(1)−C(1)	1.739(6)
S(2)−C(6)	1.729(6)		
N(2)−Yb−N(3)	92.0(2)	N(3)−Yb−N(1)	92.4(2)
N(3)−Yb−N(5)	170.2(2)	N(2)−Yb−N(4)	137.1(2)
N(1)−Yb−N(4)	81.4(2)	N(2)−Yb−S(1)	82.89(13)
N(3)−Yb−S(1)	94.32(12)	N(5)−Yb−S(1)	92.36(13)
N(4)−Yb−S(1)	139.96(13)	S(1)−Yb−S(2)	139.97(5)
N(3)−Yb−S(2)	92.13(12)	N(5)−Yb−S(2)	87.39(13)

Table 4. Significant Bond Lengths (Å) and Angles (deg) for **5**

Yb−N(1)	2.405(4)	Yb−N(3)	2.424(4)
Yb−N(3)	2.442(4)	Yb−N(5)	2.474(4)
Yb−N(5)	2.476(4)	Yb−S(1)	2.746(1)
Yb−S(3)	2.768(1)	S(1)−C(1	2.770(1)
S(1)−C(1)	1.748(5)	S(2)−C(6)	1.747(6)
S(3)−C(11)	1.732(5)		
N(1)−Yb−N(2)	70.83(14)	N(2)−Yb−N(3)	142.13(13)
N(2)−Yb−N(4)	137.62(14)	N(1)−Yb−N(5)	135.86(14)
N(3)−Yb−N(5)	72.65(13)	N(4)−Yb−S(2)	99.90(11)
N(3)−Yb−S(1)	82.30(10)	N(5)−Yb−S(1)	93.88(11)
N(2)−Yb−S(3)	128.56(11)	N(4)−Yb−S(3)	76.17(11)
S(1)−Yb−S(3)	141.08(4)	S(1)−Yb−S(2)	138.20(4)

Because of the small steric requirements of the chelating pyridinethiolate ligand, the Yb(III) ion in **5** has a higher coordination number than does the larger Yb(II) ion in **4** or the recently reported octahedral $Yb(SR)_3$ coordination compounds.[5] The Yb−S distances (S(1), 2.746(1) Å; S(2), 2.770(1) Å; S(3), 2.768(1) Å) fall within a narrower range of distances than did the Yb−S bond lengths in earlier Yb(III) thiolate reports but are within the range of values for terminal Yb(III) thiolates, even though both the higher coordination number and the resonance-delocalized charge might have been expected to lead to significantly longer Yb−S bonds.

Electronic Spectra. Lanthanide complexes are, in general, lightly colored because f orbitals do not interact significantly

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with the coordination sphere and f−f excitations are forbidden. Intensely colored compounds are observed, however, whenever there are low energy f^n-to-$f^{n-1}d^1$, MLCT, or LMCT excitations. The intense colors of **1**, **4**, and **5** can be assigned as such.

The Ce compound **1** is a bright orange crystalline material. When Ce(III) compounds are intensely colored, the transition is usually assigned as a promotion from an f^1 to a d^1 configuration. These excitations are intensely sensitive to ligand environment not because of any ligand−f orbital overlap but because of the extreme sensitivity of the relative energy of the excited state configuration to the identity of the coordinating ligands. The color of **1** (λ_{max} = 447 nm) is visually indistinguishable from the color of plastic materials doped with Ce_2S_3,[20] a pigment currently being developed as a nontoxic alternative to group 12 metal chalcogenide pigments.[8a,b] The color of compound **1** is also similar to that of the anionic dithiocarbamate of Ce, $Ce(S_2CNEt_2)_4^-$, which is reported to exhibit an f^1-to-d^1 promotion at 439 nm.[21]

Because both **1** and the isostructural Eu derivative were orange (the Eu color was assigned to a S-to-Eu(III) charge transfer absorption (λ_{max} = 420 nm)[2]), it was important to establish that the color was not a purely ligand-based electronic transition. For this reason, the isostructural Tm(III) and Ho derivatives $(PEt_4)(Ln(SPy)_4)$ [Ln = Tm (**2**), Ho (**3**)] were prepared in a fashion identical to the synthesis of **1**. Both **2** and **3** crystallize initially as blocks and then as long colorless needles, but both are indeed isostructural with the Eu derivative, on the basis of single-crystal diffraction data.[2] The absence of color in **2** and **3** supports the assignments of the Eu and Ce electronic spectra.

Both Yb compounds **4** and **5** are intensely colored. The Yb(II) derivative **4** also has a relatively low-energy f-to-d promotion in the visible spectrum, along with a broader Yb-to-pyridine charge transfer excitation. The low energy of the latter excitation suggests that this compound will have reactivity that parallels the one-electron-reduction chemistry of Sm(II).[6] If Ln-to-py charge transfer energy is an accurate reflection of the reducing potential of Ln(II) ions, then $Yb(SPy)_2$ will be as strong a reducing agent as Sm(II), since the Yb−py CT energy (eV) is similar to the Sm-to-py charge transfer energy.[22] The ease with which **4** can be prepared and crystallized, coupled with the smaller metal size (and thus presumably greater control of reactivity), makes this molecule an attractive alternative to Sm(II)-based reagents.

The ability of the SPy ligand to stabilize higher oxidation states is clearly evident in the absorption energy of both **4** and **5**. In divalent **4**, the Yb-to-py charge transfer is considerably lower in energy (667 nm) than is the corresponding transition in the benzenethiolate complex $(py)_4Yb(SPh)_2$ (577 nm),[18] and this lower energy can be interpreted as the SPy ligand either increasing electron density on the Yb(II) ion or preferentially stabilizing the Yb(III) excited state. In trivalent complexes, the LMCT energy in **5** (377 nm) is shifted to higher energy relative to $(py)_3Yb(SPh)_3$ (470 nm).[5a] These differences can be interpreted either as considering the SPy anion to be more electronegative (relative to SPh) or by suggesting that the difference between Yb(II) and Yb(III) energy levels is greater in SPy chemistry because the SPy ligand is more effective in stabilizing the Yb(III) oxidation state. Both observations are consistent with the conclusion, drawn originally from observations in related $Eu(SPy)_x$ chemistry,[2] that the SPy ligand stabilizes higher Ln oxidation states more effectively than does SPh.

Conclusions

The pyridinethiolate ligand can be used to form stable isolable complexes with both early and late lanthanides. The ligand is capable of stabilizing all Ln(III) ions but will not form a stable Ce(IV) complex. The larger ions form relatively insoluble complexes that can be solubilized with additional SPy anion, while the smaller lanthanides become increasingly more soluble, to the point that they can be crystallized from neutral organic donor solvents.

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Supporting Information Available: Tables listing structure refinement details, atomic positional parameters, bond lengths and angles, and least-squares planes and fully labeled ORTEP diagrams for **1**, **4**, and **5** (28 pages). Ordering information is given on any current masthead page.

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