5396 *Inorg. Chem.* **1998,** *37,* 5396−5398

Lanthanide Tris(*tert*-butylthiolates) and the Crystal Structure of $[\mathrm{Yb(SBu^t)_2(\mu_2\text{-}SBu^t)(Bipy)}]_2$

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Received January 22, 1998

Introduction

Lanthanide sulfides have recently been identified as an emerging class of optical materials.[1] Synthesis of these materials can, however, be problematic; the lanthanides are all highly oxophilic, and extreme conditions are required to introduce sulfur into the primary coordination sphere of the lanthanide when traditional O-bonded compounds such as lanthanide oxide or carbonate are used as starting materials. The search for S-bonded complexes as precursors to lanthanide sulfides has prompted a growing interest in lanthanide thiolates in recent years. Although trivalent lanthanide ions generally behave as hard Lewis acids and are not renowned for their propensity to bind to soft S-donor ligands, S-bonded complexes such as dithiocarbamates[2] and dithiophosphinates[3] have been known for some time. The first structurally characterized lanthanide thiolate complexes were reported in 1985,[4] and since then, several other lanthanide thiolates have been prepared. Most of the known lanthanide tris(thiolates) have arylthiolate ligands,[5] and substituents such as $\mathrm{Pr^i}$ [6] or $\mathrm{Bu^t}$ [7] in the 2 and 6 positions have been used to increase the bulk of the ligand and thus prevent polymer formation. In contrast, the chemistry of lanthanides with alkylthiolates has been much less explored, one very recent example being complexes of Y with the $\mathrm{SC(Et)_3}$ ligand.[8] In this paper, we report the preparation of lanthanide tris(*tert*-butylthiolates) and the crystal structure of $[\mathrm{Yb(SBu^t)_2(\mu_2\text{-}SBu^t)(bipy)}]_2$.

Results and Discussion

Lanthanide thiolates have been prepared by metathesis of a lanthanide halide with an alkali metal thiolate,[9] by oxidative addition of disulfide RSSR to lanthanide metal,[10] and by protonolysis of a reactive lanthanide complex with thiol.[7] Metathesis reactions in lanthanide chemistry are frequently plagued by retention of alkali metal and/or halide in the product, and we therefore chose the protonolysis of the readily available lanthanide tris(silylamides) $[\mathrm{Ln\{N(SiMe_3)_2\}_3}]$ with $\mathrm{Bu^tSH}$ as a convenient route to $[\mathrm{Ln(SBu^t)_3}]$. The $\mathrm{(Me_3Si)_2NH}$ produced during the reaction is volatile and readily removed in vacuo. Reaction of $[\mathrm{Ln\{N(SiMe_3)_2\}_3}]$ (Ln = Ce, Pr, Nd, Eu, Yb, Y) with 3 equiv of $\mathrm{Bu^tSH}$ in toluene led to rapid formation of a precipitate analyzing as $[\mathrm{Ln(SBu^t)_3}]$, which was totally insoluble in noncoordinating solvents and which we presume to be polymeric.

We aimed to prepare soluble molecular complexes and therefore carried out the reaction using THF as the solvent with the hope of isolating a soluble THF adduct. When the reaction was carried out in THF, immediate precipitation of polymeric $[\mathrm{Ln(SBu^t)_3}]$ occurred for the early lanthanides Ce and Pr. For the later lanthanides Eu−Yb and Y, no precipitation was observed from THF, indicating that a molecular species $[\mathrm{Ln(SBu^t)_3(THF)}_n]$ was formed. Nd showed intermediate behavior with incomplete precipitation of $[\mathrm{Nd(SBu^t)_3}]$. In the cases of Eu and Yb, color changes (to very deep red and orange, respectively) were observed on addition of $\mathrm{Bu^tSH}$, and ^{1}H NMR spectroscopy of reactions carried out in THF-d_8 (Ln = Y, Yb) indicated that complete displacement of $\mathrm{N(SiMe_3)_2}$ ligands had occurred. However, the THF was only very weakly coordinated and attempts to isolate the THF adduct resulted only in formation of $[\mathrm{Ln(SBu^t)_3}]$, as shown by elemental analysis.

It became clear that a more strongly binding ligand than THF would be required in order to form a stable molecular complex, and we next attempted to incorporate the pentadentate tetraglyme $\mathrm{CH_3O(CH_2CH_2O)_4CH_3}$ into the thiolate complexes. However, although tetraglyme will coordintate to lanthanide aryloxides[11] and β-diketonates,[12] we were unable to incorporate this ligand into any of the $\mathrm{Bu^tS}$ complexes, and as expected, diglyme was similarly unsuccessful. Pyridine has been used to prepare monomeric lanthanide thiophenolates;[5b] however, we were unable to form soluble adducts on addition of 3 equiv of pyridine to toluene suspensions of $[\mathrm{Ln(SBu^t)_3}]$, although we were, eventually, able to dissolve these compounds in neat pyridine, presumably to form $[\mathrm{Ln(SBu^t)_3(py)}_n]$. Pyridine dissociated rapidly unless present in excess, and only $[\mathrm{Ln(SBu^t)_3}]$ could be isolated.

We next tried 2,2′-dipyridyl (bipy) in the hope that the chelate effect would lead to formation of stable adducts. In the case of Ln = Y or Yb, addition of 1 equiv of bipy and 3 equiv of $\mathrm{Bu^tSH}$ to a toluene solution of $[\mathrm{Ln\{N(SiMe_3)_2\}_3}]$ led to formation of crystals (yellow for Y, deep orange for Yb). In the case of Ln = Yb, the crystals were shown by X-ray diffraction to be $[\mathrm{Yb(SBu^t)_2(\mu_2\text{-}SBu^t)(bipy)}]_2$. In the case of Ln = Nd or Eu, reaction under these conditions resulted only in formation of impure $[\mathrm{Ln(SBu^t)_3}]_n$ containing very small, nonstoichiometric quantities of bipy; reaction in the presence of 2 equiv of bipy gave similar results. We were unable to isolate any analogous complexes with phenanthroline.

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S0020-1669(98)00068-8 CCC: $15.00

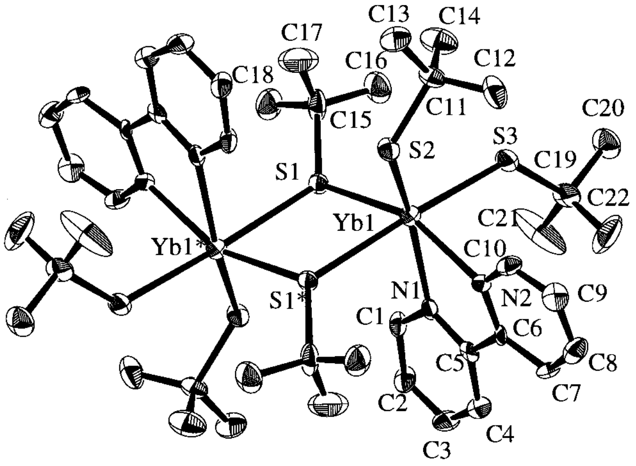

Figure 1. ORTEP plot (at the 50% probability level) of [Yb(SBu^t)$_2$-(μ_2-SBu^t)(bipy)]$_2$. H atoms are omitted for clarity. Atoms Yb1* and S1* are related by a center of symmetry to Yb1 and S1, respectively.

NMR spectroscopy of [Yb(SBu^t)$_2$(μ_2-SBu^t)(bipy)]$_2$ gave no useful information about the solution structure of this paramagnetic complex. The ^{1}H NMR spectrum of the corresponding Y complex in THF-d$_8$ showed a single resonance for SBu^t and broadened resonances due to rapidly exchanging free and coordinated THF, indicating that the dimer is cleaved to form monomeric [Y(SBu^t)$_3$(bipy)(THF)$_n$] in solution.

Bipy dissociates very readily from [Yb(SBu^t)$_2$(μ_2-SBu^t)-(bipy)]$_2$; when a sample in an evacuated tube (ca. 10^{-3} mmHg) was warmed to ca. 40 °C it began to lose its deep orange color, and colorless crystals, shown by elemental analysis to be bipy, formed in the cool part of the tube. It is quite remarkable that bipy, normally considered to be a strongly bound ligand, will dissociate under such mild conditions; in the related complex [Yb(SPh)$_3$(py)$_3$] pyridine dissociates at 80−100 °C in vacuo.[5b] The potential of [Ln(SBu^t)$_3$] as precursors to lanthanide sulfides is currently under investigation.

Crystal Structure of [Yb(SBu^t)$_3$(bipy)]$_2$·2THF

Crystals of this complex suitable for X-ray diffraction were grown from THF/petroleum ether; the THF molecules were not coordinated to Yb and were lost very rapidly in the absence of solvent. An ORTEP plot of the complex is shown in Figure 1, and selected bond lengths and angles are presented in Table 1. The complex is a centrosymmetric dimer, with the two approximately octahedrally coordinated Yb atoms bridged by two μ_2-SBu^t groups. The bipy ligand is almost planar, having a torsion angle of 7° about the C−C bond. The only other example of an alkylthiolate-bridged Yb dimer is [Cp$_2$Yb(μ_2-SBu^n)]$_2$, in which the Yb−Yb distance is 3.974 Å and the Yb−μ_2-S distances are 2.716 and 2.699 Å.[13] The average Yb−N distance in [Yb(SPh)$_3$(py)$_3$] is 2.453 Å,[10] and that in [Yb(S-2, 4, 6-Pr$^i_3$C$_6$H$_2$)$_3$(py)$_3$] is 2.409 Å.[6] The only bipy complex of Yb in the Cambridge Crystallographic Data Base is [Yb(acac)$_3$-(bipy)], in which the Yb−N distances are 2.500 and 2.535 Å.[14]

Conclusions

We have prepared a series of lanthanide tris(*tert*-butylthiolates) and the first structurally characterized example of a lanthanide tris(alkylthiolate). The SBu^t ligand has been shown to have a much greater tendency than arylthiolates to form bridged, presumably polymeric complexes even in the presence of donors such as THF, tetraglyme, pyridine, and bipy. Bipy dissociates under remarkably mild conditions from [Yb(SBu^t)$_3$-(bipy)]$_2$.

Table 1. Selected Intramolecular Distances (Å) and Angles (deg) for [Yb(SBu^t)$_3$(bipy)]$_2$[a]

Yb(1)−Yb(1)*	4.337(3)
Yb(1)−S(1)	2.707(3)
Yb(1)*−S(1)	2.788(2)
Yb(1)−S(2)	2.620(3)
Yb(1)−S(3)	2.627(3)
Yb(1)−N(1)	2.414(8)
Yb(1)−N(2)	2.409(7)
S(1)−Yb(1)−S(1)	75.78(8)
S(1)−Yb(1)−S(2)	103.72(8)
S(1)−Yb(1)−S(3)	102.99(9)
S(1)−Yb(1)−S(2)	82.86(8)
S(1)−Yb(1)−S(3)	175.47(8)
S(2)−Yb(1)−S(3)	101.67(9)
Yb(1)−S(1)−Yb(1)*	104.22(8)
S(1)−Yb(1)−N(1)	91.6(2)
S(1)−Yb(1)−N(2)	157.0(2)
S(1)−Yb(1)−N(1)	82.7(2)
S(1)−Yb(1)−N(2)	92.7(2)
S(2)−Yb(1)−N(1)	155.6(2)
S(2)−Yb(1)−N(2)	94.3(2)
S(3)−Yb(1)−N(1)	93.0(2)
S(3)−Yb(1)−N(2)	86.9(2)
N(1)−Yb(1)−N(2)	66.8(2)
Yb(1)−S(1)−C(15)	120.0(3)
Yb(1)*−S(1)−C(15)	125.7(3)
Yb(1)S(2)−C(11)	120.4(3)
Yb(1)−S(3)−C(19)	126.7(3)

[a] Atoms Yb1* and S1* are related by a center of symmetry to atoms Yb1 and S1, respectively.

Experimental Section

All the preparations described below were performed under strictly anaerobic conditions using standard Schlenk techniques. Solvents were distilled from sodium/benzophenone ketyl (nondeuterated) or CaH$_2$ (deuterated) and stored under N$_2$ over 4 Å molecular sieves prior to use. Samples for NMR spectroscopy were sealed under vacuum, and spectra were recorded on Bruker WM250 or AC200 spectrometers. Elemental analyses were performed in duplicate by Mr. S. Apter of this department. For S analysis, the sample was transferred in the drybox into a gelatin capsule. The sample was burned in O$_2$, and the combustion products were absorbed into dilute H$_2$O$_2$ solution over a period of 18 h. Excess H$_2$O$_2$ was removed by evaporation, and the sample was dissolved in H$_2$O/Pr^{i}OH. A slight excess (with respect to Ln^{3+}) of DTPA (diethylenetriaminepentaacetic acid) was added, and the solution was left at room temperature for several hours before titration with standard barium perchlorate solution. In the absence of DTPA, no BaSO$_4$ was precipitated; this was due to the formation of [Ln(SO$_4$)$_3$]$^{3-}$. (For [Ce(SO$_4$)$_3$]$^{3-}$ log $\beta_3 = 3.29$,[15] and for [Eu(SO$_4$)$_3$]$^{3-}$ log $\beta_3 = 5.09$.[16])

Preparation of [Ln(SBu^t)$_3$]. [Ln{N(SiMe$_3$)$_2$}$_3$] (1.3 mmol) was dissolved in toluene (ca. 25 cm^3). To this solution was added Bu^{t}SH (4 mmol) (Stench!). The product was precipitated as a powdery solid after ca. 5 min at room temperature. The supernatant solution was removed by decantation and the solid product was dried in vacuo. Typical isolated yield = 90%. All products are air and moisture sensitive; [Ce(SBu^t)$_3$] and [Eu(SBu^t)$_3$] were pyrophoric. Analytical data and colors of products (in parentheses) are as follows. [La(SBu^t)$_3$] (white) Found: C, 38.36; H, 6.55; S, 21.95%. Calcd for C$_{12}$H$_{27}$S$_3$La: C, 35.46; H, 6.70; S, 23.66%. [Ce(SBu^t)$_3$] (yellow, pyrophoric) Found: C, 34.62; H, 6.56%. Calcd for C$_{12}$H$_{27}$S$_3$Ce: C, 35.63; H,

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Table 2. Crystallographic Data for $[Yb(SBu^t)_2(\mu_2\text{-}SBu^t)(bipy)]_2 \cdot 2THF$

Crystal Data	
empirical formula	$C_{22}H_{35}N_2S_3OYb$
formula weight	612.75
crystal system	monoclinic
space group	$P2_1/n$ (no. 14)
lattice parameters:	
a, Å	12.061(8)
b, Å	15.856(6)
c, Å	15.456(7)
β, deg	95.98(4)
V, Å^3	2940(2)
Z	2
D_{calc}, g cm^{-3}	1.384
F_{000}	1228
μ(Mo Kα), cm^{-1}	33.90
Intensity Measurements	
diffractometer	Rigaku AFC6S
radiation	Mo Kα ($\lambda = 0.710\ 69$ Å)
temperature, °C	−120
takeoff angle, deg	6.0
detector aperture, mm	
horizontal	6.0
vertical	6.0
crystal-to-detector distance, cm	40
scan type	$\omega - 2\theta$
scan rate, deg min^{-1}	4 (in ω), 2 rescans
scan width, deg	$(1.05 + 0.30 \tan \theta)$
$2\theta_{max}$, deg	50.0
no. of reflections measured	
total	5664
unique	5395 ($R_{int} = 0.043$)
corrections	Lorentz-polarization absorption (trans. factors: 0.92−1.02)
Structure Solution and Refinement	
structure solution	direct methods
hydrogen atom treatment	included in calcd positions ($d_{C-H} = 0.95$ Å)
refinement	full-matrix least-squares
function minimized	$\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2$
least-squares weights	$4F_o^2/\sigma^2(F_o^2)$
p-factor	0.03
anomalous dispersion	all non-hydrogen atoms
no. observations ($I > 3.00\sigma(I)$)	3179
no. variables	273
reflection/parameter ratio	11.64
residuals: R; R_w	0.038; 0.040
goodness of fit indicator	1.16
max shift/error in final cycle	0.03
max peak in final diff. map, e/Å^3	0.64
min. peak in final diff. map, e/Å^3	−0.81

6.68%. $[Pr(SBu^t)_3]$ (pale green) Found: C, 35.22; H, 6.71%. Calcd for $C_{12}H_{27}S_3Pr$: C, 35.29; H, 6.66%. $[Nd(SBu^t)_3]$ (pale blue) Found: C, 34.80; H, 6.70%. Calcd for $C_{12}H_{27}S_3Nd$: C, 35.00; H, 6.61%. $[Eu(SBu^t)_3]$ (deep red-brown, pyrophoric) Found: C, 31.31; H, 5.95%. Calcd for $C_{12}H_{27}S_3Eu$: C, 34.36; H, 6.49%. $[Yb(SBu^t)_3]$ (orange) Found: C, 32.23; H, 6.23%. Calcd for $C_{12}H_{27}S_3Yb$: C, 32.71; H, 6.18%. $[Y(SBu^t)_3]$ (white) Found: C, 39.29; H, 5.91; S, 29.61%. Calcd for $C_{12}H_{27}S_3Y$: C, 40.43; H, 6.18; S, 24.94%.

NMR Tube Reaction of $[Yb\{N(SiMe_3)_2\}_3]$ with Bu^tSH. $[Yb\{N(SiMe_3)_2\}_3]$ (0.112 g, 0.17 mmol) was placed in a 5 mm NMR tube attached to a right-angled PTFE stopcock. THF-d_8 (0.5 cm^3) was added to give a clear yellow solution. Bu^tSH (59 μL, 0.514 mmol) was then added and the tube was sealed in vacuo. A deep orange-red coloration developed immediately on addition of Bu^tSH. A ^{1}H NMR spectrum recorded after 2 h at room temperature showed the presence of $HN(SiMe_3)_2$ and no $[Yb\{N(SiMe_3)_2\}_3]$. Resonances due to SBu^{t-} bonded to Yb could not be identified. An analogous reaction between $[Y\{N(SiMe_3)_2\}_3]$ and Bu^tSH showed resonances at δ 0.116 (HN(Si*Me*$_3$)$_2$ and 1.467 (YS*Bu*^{t}). A very low intensity resonance at δ 0.226 was due to a small quantity of unreacted $[Y\{N(SiMe_3)_2\}_3]$. Broad resonances at δ 1.90 and δ 3.75 were due to rapidly exchanging free and coordinated THF.

Preparation of $[Yb(SBu^t)_2(\mu\text{-}SBu^t)(bipy)]_2$. $[Yb\{N(SiMe_3)_2\}_3\}]$ (0.960 g, 1.467 mmol) was dissolved in toluene (20 cm^3). To this solution was added bipy (0.229 g, 1.467 mmol) in toluene (12 cm^3), followed by Bu^tSH (0.50 cm^3, 4.40 mmol). After about 5 min, the reaction mixture had become orange in color. Stirring at room temperature was continued for 30 min; after which time, the reaction mixture was allowed to stand, and a small amount of pale yellow solid settled out. The clear orange solution was decanted into a clean flask. On standing at room temperature overnight, orange crystals had formed. The reaction mixture was cooled to −18 °C to ensure complete crystallization of the product. The very pale orange supernatant was decanted off and the bright orange crystals were dried briefly in vacuo. Yield: 0.564 g (64%). Anal. Calcd for $C_{44}H_{74}N_4Yb_2$: C, 44.13; H, 6.23; N, 4.68%. Found: C, 45.99; H, 5.96; N, 4.46%. $[Y(SBu^t)_2(\mu_2\text{-}SBu^t)(bipy)]_2$ was prepared in an analogous manner and precipitated as pale yellow crystals. Anal. Calcd. for $C_{44}H_{74}N_4Y_2$: C, 51.55; H, 6.88; N, 5.46%. Found: C, 53.82; H, 7.01; N, 6.03%. ^{1}H NMR (d_8-THF): 1.389 (s, 27H, S*Bu*^{t}); 1.72, 3.57 (br, THF); 7.29 (m, 2H), 7.81 (m, 2H), 8.49 (m, 2H), 8.61 (m, 2H, bipy).

X-ray Data Collection, Structure Determination, and Refinement for $[Yb(SBu^t)_2(\mu_2\text{-}SBu^t)(bipy)]_2 \cdot 2THF$. Crystals of $[Yb(SBu^t)_2(\mu_2\text{-}SBu^t)(bipy)]_2 \cdot 2THF$ were grown at room temperature from THF/petroleum ether. An orange plate of approximate dimensions 0.2 mm × 0.05 mm × 0.35 mm was mounted on a glass fiber in Nujol oil and cooled to −120 °C in a stream of N_2 gas. The cell constants were obtained from 19 carefully centered reflections in the range $6.84 < 2\theta < 11.09°$. Crystal data and details of data collection are summarized in Table 2. An empirical absorption correction was applied based on ψ scans. The structure was solved by direct methods (SHELXS-86). Data reduction and all other calculations were performed using the TEXSAN suite of programs.[17]

Acknowledgment. We are grateful to EPSRC and Rhône-Poulenc for financial support (CASE award to S.A.C.), to Mr. J. V. Barkley for X-ray data collection, and to Mr. S. Apter for elemental analyses.

Supporting Information Available: A listing of experimental details, positional and thermal parameters, intramolecular bond distances and angles, and torsional angles (15 pages). Ordering information is given on any current masthead page.

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