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Homoleptic 2-Mercapto Benzothiazolate Uranium and Lanthanide Complexes

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Treatment of [$Ln(BH_4)_3(THF)_3$] (Ln = Ce, Nd) with 3 and 4 mol equiv of KSBT in tetrahydrofuran (THF) led to the formation of [$Ln(SBT)_3(THF)$] and [$K(THF)Ln(SBT)_4$], respectively. The uranium(IV) compound [$U(SBT)_4(THF)_2$] was obtained from $U(BH_4)_4$ and was reversibly reduced by sodium amalgam into the corresponding anionic uranium(III) complex. The crystal structures of [$Ln(SBT)_3(THF)_2$] (Ln = Ce, Nd), [K(15-crown-5)$_2$][$Nd(SBT)_4$], [$U(SBT)_4(THF)$], and [K(15-crown-5)$_2$][$U(SBT)_4(py)$] show the bidentate coordination mode and the thionate character of the SBT ligand.

Introduction

Main group and transition metal complexes with the 2-mercapto benzothiazolate ligand (SBT) are interesting for their structural and reactivity features[1] and have received special attention for their biological activity[2] and their application as anticorrosion agents and accelerators in the rubber vulcanization processes.[3] As a heterocyclic thionate ligand with potential S and N donors, the SBT ligand in mononuclear complexes can adopt multifunctional coordination modes—unidentate-N, unidentate-$S_{exocyclic}$, and bidentate-S,N—and can act in polynuclear complexes as a bridging ligand between two,[4a] three,[4b] and even four metal centers;[4c] the presence of N and S atoms of distinct softness favors the building of hetero or homopolynuclear complexes with the metals in different oxidation states.

In contrast, the SBT ligand was almost ignored in f-element chemistry, the compounds being limited essentially to the lanthanide complexes [$Ln(C_5H_4R)_2(SBT)(THF)$] (R = H and Ln = Y, Sm, Dy, Yb,[5a] and Tm;[5b] R = $SiMe_2{}^tBu$ and Ln = Er[6]). We recently enlarged this family of organometallic compounds with the uranium(IV) derivatives [$U(Cp^*)_2(SBT)_2$] and [$U(Cp^*)(SBT)_3$] (Cp* = η-C_5Me_5), and the trivalent complexes [$M(Cp^*)(SBT)_3$]$^-$ (M = U, La, Ce, Nd).[7] In these pentagonal bipyramidal complexes, the peculiar behavior of the axial M−N bond gave a first evidence of the presence of a specific covalent binding site in discriminating between lanthanide(III) and actinide(III) complexes.

Following these studies, it seemed to us interesting to see if the SBT ligand, in contrast to the dithiolene[8] and thiolate ligands,[9] could give easily accessible and thermally stable homoleptic complexes of uranium(III). The only inorganic SBT complexes of the f-elements so far reported are [$Ln(SBT)Cl_2$][$Ln(OH)_3$]$\cdot xH_2O$[10] and [$Th(SBT)_4$],[11] which were characterized by their elemental analyses and IR

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spectra. Here we present the synthesis and X-ray crystal structures of the homoleptic SBT complexes and/or their Lewis base adducts $[Ln(SBT)_3L_n]$, $[Ln(SBT)_4]^-$ (Ln = Ce, Nd; L = THF or py), $[U(SBT)_4(THF)]$, and $[U(SBT)_4(py)]^-$.

Experimental Section

All reactions were carried out under argon with the rigorous exclusion of air and water (<5 ppm oxygen or water) using standard Schlenk-vessel and vacuum line techniques or in a glovebox. Solvents were thoroughly dried by standard methods and distilled immediately before use. The ^{1}H NMR spectra were recorded on a Bruker DPX 200 instrument and referenced internally using the residual protio solvent resonances relative to tetramethylsilane (δ 0); the spectra were recorded at 23 °C when not otherwise specified. Elemental analyses were performed by Analytische Laboratorien at Lindlar (Germany). HSBT, 15-crown-5, and 18-crown-6 (Fluka) were dried under vacuum before use. KSBT,[7] $[M(BH_4)_3(THF)_3]$ (M = Ce,[12] Nd,[13] U[14]), $[U\{N(SiMe_3)_2\}_3]$,[15] $[UI_3(THF)_4]$,[15] and $U(BH_4)_4$[16] were synthesized as previously reported.

Synthesis of $[Ce(SBT)_3(THF)]$. A solution of KSBT (339 mg, 1.65 mmol) in THF (20 mL) was added dropwise into a flask containing a solution of $[Ce(BH_4)_3(THF)_3]$ (219 mg, 0.55 mmol) in THF (30 mL). After 2 h at 20 °C, the reaction mixture was filtered to remove the KBH_4 precipitate, the solvent was evaporated off, and the yellow powder of $[Ce(SBT)_3(THF)]$ was dried under vacuum. Yield: 391 mg (99%). Anal. Calcd for $C_{25}H_{20}N_3OS_6Ce$: C, 42.23; H, 2.84; N, 5.91; S, 27.06. Found: C, 41.81; H, 2.66; N, 5.93; S, 26.78. This powder is insoluble in THF; the ^{1}H NMR spectra were recorded before evaporation of a freshly prepared solution of $[Ce(SBT)_3(THF)_x]$. ^{1}H NMR (THF-d_8, −85 °C): δ 13.29, 9.81, 8.91, and 8.69 (s, 4 × 3H, SBT). Yellow crystals of $[Ce(SBT)_3(THF)_2]$ suitable for X-ray diffraction were obtained by slow diffusion of pentane into a THF solution.

Synthesis of $[Nd(SBT)_3(THF)]$. An NMR tube was charged with $[Nd(BH_4)_3(THF)_3]$ (6.0 mg, 0.015 mmol) in THF-d_8 (0.4 mL) and KSBT (9.0 mg, 0.045 mmol) was added to the solution. After 1 h at 20 °C, the spectrum of the blue solution showed the quantitative formation of $[Nd(SBT)_3(THF)_x]$. ^{1}H NMR (THF-d_8, −70 °C): δ 12.87, 11.40, 9.82, and 8.83 (s, 4 × 3H, SBT). Blue crystals of $[Nd(SBT)_3(THF)_2]$ suitable for X-ray diffraction were obtained by slow diffusion of pentane into the THF solution.

Synthesis of $[Ce(SBT)_3(py)_4]$. An NMR tube was charged with $[Ce(SBT)_3(THF)]$ (ca. 10 mg) in pyridine (0.4 mL). The yellow solution was evaporated to dryness, leaving a yellow powder of $[Ce(SBT)_3(py)_4]$. ^{1}H NMR (THF-d_8): δ 10.59 (s, 3H, SBT), 8.92 (s, 3H, SBT), 8.59 (s, 3H, SBT), 8.48 (m, 8H, py), 7.98 (s, 3H, SBT), 7.66 (m, 4H, py), 7.25 (m, 8H, py).

Synthesis of $[Nd(SBT)_3(py)_4]$. KSBT (131 mg, 0.64 mmol) was added to a solution of $[Nd(BH_4)_3(THF)_3]$ (85 mg, 0.21 mmol) in THF (30 mL). After 1 h at 20 °C, the reaction mixture was filtered to remove the KBH_4 precipitate, and the blue solution was evaporated to dryness. The residue was extracted with pyridine (20 mL), and after evaporation of the solvent, the blue powder of $[Nd(SBT)_3(py)_4]$ was dried under vacuum. Yield: 115 mg (57%). Anal. Calcd for $C_{41}H_{32}N_7S_6Nd$: C, 51.33; H, 3.36; S, 20.05. Found: C, 51.19; H, 3.21; S, 19.80. ^{1}H NMR (THF-d_8): δ 10.58 (s, 3H, SBT), 9.78 (s, 3H, SBT), 8.52 (s, 3H, SBT), 8.42 (m, 8H, py), 8.02 (s, 3H, SBT), 7.66 (m, 4H, py), 7.25 (m, 8H, py).

Synthesis of $[K(THF)Ce(SBT)_4]$. A solution of KSBT (534 mg, 2.60 mmol) in THF (20 mL) was added dropwise into a solution of $[Ce(BH_4)_3(THF)_3]$ (262 mg, 0.65 mmol) in THF (30 mL). After 2 h at 20 °C, the reaction mixture was filtered to remove the KBH_4 precipitate, the solvent was evaporated off and the yellow powder of $[K(THF)Ce(SBT)_4]$ was dried under vacuum. Yield: 590 mg (99%). Anal. Calcd for $C_{32}H_{24}N_4OS_8KCe$: C, 41.95; H, 2.64; N, 6.11; S, 28.00. Found: C, 41.60; H, 2.54; N, 6.09; S, 27.73. This powder is insoluble in THF; the ^{1}H NMR spectra were recorded before evaporation of a freshly prepared solution of $[K(THF)_x\text{-}Ce(SBT)_4]$. ^{1}H NMR (THF-$d_8$, −70 °C): δ 9.40, 8.91, 8.08, and 7.66 (s, 4 × 4H, SBT).

Synthesis of $[K(THF)Nd(SBT)_4]$. An NMR tube was charged with $[Nd(BH_4)_3(THF)_3]$ (6.0 mg, 0.015 mmol) in THF-d_8 (0.4 mL) and KSBT (12.0 mg, 0.060 mmol) was added to the solution. After 1 h at 20 °C, the spectrum of the blue solution showed the quantitative formation of $[K(THF)_xNd(SBT)_4]$. ^{1}H NMR (THF-d_8, −70 °C): δ 10.08, 9.44, 7.99, and 7.61 (s, 4 × 4H, SBT).

Synthesis of $[K(py)_4Ce(SBT)_4]$. An NMR tube was charged with $[K(THF)Ce(SBT)_4]$ (ca. 10 mg) in pyridine (0.4 mL). The yellow solution was evaporated to dryness, leaving a yellow powder of $[K(py)_4Ce(SBT)_4]$. ^{1}H NMR (THF-d_8): δ 9.51 (s, 4H, SBT), 8.54 (m, 8H, py), 8.16 (s, 4H, SBT), 7.66 (m, 4H, py), 7.56 (s, 4H, SBT), 7.46 (s, 4H, SBT), 7.25 (m, 8H, py).

Synthesis of $[K(py)_4Nd(SBT)_4]$. KSBT (132 mg, 0.64 mmol) was added to a solution of $[Nd(BH_4)_3(THF)_3]$ (65 mg, 0.16 mmol) in THF (30 mL). After 1 h at 20 °C, the reaction mixture was filtered to remove the KBH_4 precipitate, and the blue-green solution was evaporated to dryness. The residue was extracted with pyridine (30 mL) and after evaporation of the solvent, the blue powder of $[K(py)_4Nd(SBT)_4]$ was dried under vacuum. Yield: 177 mg (95%). Anal. Calcd for $C_{48}H_{36}N_8S_6KNd$: C, 49.50; H, 3.12; N, 9.62; S, 22.02. Found: C, 49.29; H, 3.07; N, 9.81; S, 22.27. ^{1}H NMR (THF-d_8, −70 °C): δ 10.14 (s, 4H, SBT), 9.27 (s, 4H, SBT), 8.54 (m, 8H, py), 8.00 (s, 4H, SBT), 7.72 (s, 4H, py), 7.57 (s, 4H, SBT), 7.32 (m, 8H, py).

Crystals of $[K(15\text{-crown-}5)_2][Nd(SBT)_4]$. An NMR tube was charged with $[Nd(BH_4)_3(THF)_3]$ (6.0 mg, 0.016 mmol) and KSBT (13.0 mg, 0.064 mmol) in pyridine (0.4 mL). After 2 h at 20 °C, 15-crown-5 (7.0 mg, 0.032 mmol) was added to the blue solution. Slow diffusion of pentane into the solution led to the formation of blue crystals of $[K(15\text{-crown-}5)_2][Nd(SBT)_4]$ suitable for X-ray diffraction.

Synthesis of $[U(SBT)_4(THF)_2]$. A flask was charged with $U(BH_4)_4$ (134 mg, 0.45 mmol) and KSBT (370 mg, 1.80 mmol), and THF (20 mL) was condensed in it. After 1 h at 20 °C, the reaction mixture was filtered to remove the KBH_4 precipitate, the orange solution was evaporated to dryness, and the orange powder of $[U(SBT)_4(THF)_2]$ was dried under vacuum. Yield: 453 mg (96%). Anal. Calcd for $C_{36}H_{32}N_4O_2S_8U$: C, 41.29; H, 3.08; N, 5.35; S, 24.50. Found: C, 41.01; H, 3.23; N, 5.52; S, 24.48. ^{1}H NMR (pyridine-d_5): δ 11.53, 8.42, 7.68, and 7.22 (s, 4 × 4H, SBT), 3.67 and 1.63 (m, 2 × 8H, THF). Brown crystals of $[U(SBT)_4(THF)]$ suitable for X-ray diffraction were obtained by slow diffusion of pentane into a THF solution.

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Table 1. Crystal Data and Structure Refinement Details

	$[Ce(SBT)_3(THF)_2]$	$[Nd(SBT)_3(THF)_2]$	$[K(15\text{-crown-}5)_2][Nd(SBT)_4]$	$[U(SBT)_4(THF)]$	$[K(15\text{-crown-}5)_2][U(SBT)_4(py)]$
empirical formula	$C_{29}H_{28}CeN_3O_2S_6$	$C_{29}H_{28}N_3NdO_2S_6$	$C_{48}H_{56}KN_4NdO_{10}S_8$	$C_{32}H_{24}N_4OS_8U$	$C_{53}H_{61}KN_5O_{10}S_8U$
M_r	783.02	787.14	1288.79	975.06	1461.68
cryst syst	triclinic	triclinic	monoclinic	triclinic	orthorhombic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1$	$P\bar{1}$	$P2_12_12_1$
a, Å	9.9378(6)	8.3567(6)	20.3792(8)	12.4133(2)	12.4896(9)
b, Å	10.6498(5)	10.2424(7)	14.6056(6)	15.8993(3)	12.8139(10)
c, Å	16.2849(11)	19.5632(15)	20.8621(7)	17.3458(4)	37.4852(16)
α, deg	75.919(4)	96.306(4)	90	82.419(1)	90
β, deg	81.390(3)	99.047(3)	113.780(2)	86.331(1)	90
γ, deg	67.307(4)	107.241(4)	90	80.565(1)	90
V, Å^3	1539.31(16)	1557.5(2)	5682.4(4)	3344.44(11)	5999.2(7)
Z	2	2	4	4	4
D_{calcd}, g cm^{-3}	1.689	1.678	1.506	1.937	1.618
μ (Mo Kα), mm^{-1}	1.919	2.102	1.337	5.388	3.112
$F(000)$	786	790	2636	1888	2932
no. of rflns collected	10245	10354	83824	22777	50879
no. of indep rflns	5275	5350	21357	11588	11258
no. of obsd rflns ($I > 2\sigma(I)$)	4656	4514	18018	10148	7218
R_{int}	0.038	0.052	0.063	0.036	0.082
no. of params refined	370	370	1286	829	703
R1	0.036	0.045	0.063	0.029	0.072
wR2	0.104	0.108	0.161	0.068	0.183
S	1.166	1.161	1.075	1.073	0.989
$\Delta\rho_{min}$, e Å^{-3}	−0.85	−0.64	−0.81	−0.80	−0.72
$\Delta\rho_{max}$, e Å^{-3}	1.12	1.08	1.35	0.89	1.50

Reversible Reduction of $[U(SBT)_4(THF)_2]$. An NMR tube was charged with $[U(SBT)_4(THF)_2]$ (6.0 mg, 0.006 mmol), 18-crown-6 (3.0 mg, 0.011 mmol) and 2% Na(Hg) (10 mg, 0.009 mmol of Na) in THF-d_8 (0.4 mL). The mixture was stirred for 12 h at 20 °C, and the spectrum of the brown solution showed the formation of $[Na(18\text{-crown-}6)][U(SBT)_4]$ as the major product with other unidentified compounds. ^{1}H NMR (THF-d_8, −70 °C): δ 12.06, 9.01, 6.74, and 4.99 (s, 4 × 4H, SBT), 2.90 (s, 24H, 18-crown-6). This compound was readily transformed back into $[U(SBT)_4(THF)_2]$ upon addition of AgI (2.1 mg, 0.009 mmol).

Crystals of $[K(15\text{-crown-}5)_2][U(SBT)_4(py)]$. An NMR tube was charged with $[U(SBT)_4(THF)_2]$ (9.0 mg, 0.009 mmol), 15-crown-5 (3.0 mg, 0.014 mmol) and 2% K(Hg) (15 mg, 0.008 mmol of K) in THF-d_8 (0.4 mL). The mixture was stirred for 12 h at 20 °C and the dark brown solution was filtered and evaporated to dryness. The residue was dissolved in pyridine (0.4 mL), and slow diffusion of pentane into the solution led to the formation of brown crystals of $[K(15\text{-crown-}5)_2][U(SBT)_4(py)]$ suitable for X-ray diffraction.

Crystallographic Data Collection and Structure Determination. The data were collected at 100(2) K on a Nonius Kappa-CCD area detector diffractometer[17] with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The crystals were introduced into glass capillaries with a protective "Paratone-N" oil (Hampton Research) coating. The unit cell parameters were determined from 10 frames and then refined on all data. The data (φ and ω scans with 2° steps) were processed with HKL2000.[18] The structures were solved by direct methods or by Patterson map interpretation with SHELXS97, expanded by subsequent Fourier-difference synthesis, and refined by full-matrix least-squares on F^2 with SHELXL97.[19] Absorption effects were corrected empirically with DELABS.[20] All nonhydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were introduced at calculated positions and were treated as riding atoms with an isotropic displacement parameter equal to 1.2 times that of the parent atom. Special details are as follows:

$[Ce(SBT)_3(THF)_2]$ and $[Nd(SBT)_3(THF)_2]$. Although isostructural, these two compounds present some geometric differences and the two molecules are only roughly superimposable, with deviations as large as 3 Å, particularly for the SBT molecule labeled C.

$[K(15\text{-crown-}5)_2][Nd(SBT)_4]$. The space group $P2_1/c$ was rejected on the basis of a too large number of exceptions to systematic extinctions (although rather weak reflections) and the untractable disorder of crown ethers present in this group. Some restraints on bond lengths and/or displacement parameters were applied for some badly behaving atoms, particularly in the crown ether moieties. One of the aromatic rings (F) had to be refined as an idealized hexagon.

$[K(15\text{-crown-}5)_2][U(SBT)_4(py)]$. Restraints on bond lengths and displacement parameters were applied for the very badly resolved crown ether moieties. Some short H···H contacts involving protons from the crown ethers are likely due to the imperfect location of these molecules.

Crystal data and structure refinement details are given in Table 1, and selected bond lengths and angles, in Table 2. The molecular plots were drawn with SHELXTL.[21]

Results and Discussion

Homoleptic Lanthanide Complexes and Their Lewis Base Adducts. Addition of 3 mol equiv of KSBT to $[Ln(BH_4)_3(THF)_3]$ in THF gave a yellow (Ln = Ce) or blue (Ln = Nd) solution of $[Ln(SBT)_3(THF)_x]$; after filtration and evaporation to dryness, the powder of $[Ce(SBT)_3(THF)]$ was isolated in almost quantitative yield. The insolubility of

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Table 2. Selected Bond Lengths (Å) and Angles (deg) in the Tris and Tetrakis(SBT) Complexes

compound	ligand	M−S(1)	M−N(1)	C(1)−N(1)	C(1)−S(1)	N(1)−M−S(1)
$[Ce(SBT)_3(THF)_2]$						
	A	2.9912(13)	2.568(4)	1.323(6)	1.717(5)	57.12(10)
	B	2.9269(12)	2.599(4)	1.308(6)	1.736(5)	57.74(9)
	C	2.9221(13)	2.600(4)	1.330(6)	1.711(5)	57.60(9)
	Av.	2.95(3)	2.59(2)	1.320(9)	1.721(11)	57.5(3)
$[Nd(SBT)_3(THF)_2]$						
	A	2.9424(16)	2.521(5)	1.312(8)	1.712(7)	57.60(12)
	B	2.9359(16)	2.525(5)	1.323(8)	1.728(7)	58.00(12)
	C	2.9006(16)	2.588(5)	1.327(7)	1.708(6)	58.05(11)
	Av.	2.93(2)	2.54(3)	1.321(6)	1.716(9)	57.9(2)
$[K(15\text{-crown-}5)_2][Nd(SBT)_4]$						
complex 1	A	2.937(3)	2.534(9)	1.326(15)	1.679(15)	57.5(2)
	B	2.933(3)	2.524(8)	1.325(13)	1.725(11)	57.85(18)
	C	2.932(3)	2.524(8)	1.343(12)	1.702(12)	57.05(19)
	D	2.928(3)	2.552(7)	1.300(14)	1.696(11)	58.1(2)
complex 2	E	2.940(3)	2.548(7)	1.309(12)	1.687(9)	57.25(18)
	F	2.948(2)	2.542(8)	1.317(14)	1.723(13)	57.8(2)
	G	2.921(3)	2.540(8)	1.325(13)	1.709(10)	58.18(18)
	H	2.938(2)	2.555(8)	1.312(12)	1.698(11)	58.02(19)
	Av.	2.935(8)	2.540(11)	1.320(12)	1.70(2)	57.7(4)
$[U(SBT)_4(THF)]$						
complex 1	A	2.8996(11)	2.534(4)	1.339(6)	1.697(4)	57.92(8)
	B	2.8347(10)	2.511(3)	1.319(5)	1.718(4)	58.94(8)
	C	2.8653(11)	2.535(4)	1.320(6)	1.705(5)	58.13(9)
	D	2.8601(12)	2.557(4)	1.334(6)	1.700(5)	58.15(8)
complex 2	E	2.8068(11)	2.504(4)	1.317(6)	1.715(5)	59.05(9)
	F	2.8933(11)	2.529(4)	1.325(5)	1.708(4)	58.12(8)
	G	2.8719(11)	2.541(4)	1.341(6)	1.705(5)	58.26(9)
	H	2.9008(11)	2.508(4)	1.314(6)	1.707(5)	58.10(9)
	Av.	2.87(3)	2.53(2)	1.326(10)	1.707(7)	58.3(4)
$[K(15\text{-crown-}5)_2][U(SBT)_4(py)]$						
	A	2.981(3)	2.610(12)	1.329(16)	1.704(15)	56.7(2)
	B	3.046(4)	2.609(10)	1.298(17)	1.702(18)	55.2(3)
	C	2.952(4)	2.645(11)	1.306(16)	1.694(15)	56.0(3)
	D	3.003(3)	2.647(10)	1.361(15)	1.723(14)	56.2(3)
	Av.	3.00(3)	2.63(2)	1.32(2)	1.706(11)	56.0(5)

$[Ln(SBT)_3(THF)]$ in THF likely reflects the presence of a polymeric and/or polynuclear compound.[22] However, the latter could be dissolved in pyridine, and the powders obtained after evaporation of the solvent, which analyze as $[Ln(SBT)_3(py)_4]$, are soluble in THF. Slow diffusion of pentane into a freshly prepared THF solution of $[Ln(SBT)_3(THF)_x]$ led to the formation of yellow (Ce) and blue (Nd) crystals of $[Ln(SBT)_3(THF)_2]$. These complexes are isostructural, and a view of the cerium derivative is shown in Figure 1. The metal center is surrounded by three S and three N atoms of the η^2-SBT ligands and two O atoms of the THF molecules, in a distorted dodecahedral arrangement; the two trapezia N(1A)−O(1)−N(1C)−O(2) and S(1B)−N(1B)−S(1A)−S(1C) [with rms deviations of 0.106 and 0.318 Å for Ln = Ce and 0.050 and 0.425 Å for Ln = Nd] form an angle of 89.46(6)° and 88.99(7)° for Ln = Ce and Nd, respectively. The three SBT ligands are bidentate, as found in the cyclopentadienyl complexes $[Ln(Cp^*)(SBT)_3]^-$ (Ln = La, Ce, Nd)[7] and the homoleptic compounds $[NEt_4][M(SBT)_3]$ (M = Ni,[23] Cd[3]), and in contrast to that observed in the zinc aquo complex $[N^nBu_4][Zn(SBT)_3(OH_2)]$ where two SBT ligands are coordinated via the exocyclic S atoms and the third one is attached via a bond to the nitrogen atom.[3] The Ce−X distances, which average 2.59(2) and 2.95(3) Å for X = N and S, respectively, are larger than the corresponding Nd−X distances, by about 0.02–0.05 Å, in agreement with the difference in the ionic radii of the metals.[24] The Ln−N and Ln−S bonds are about 0.04 Å shorter than those in $[Ln(Cp^*)(SBT)_3]^-$ (Ln = Ce, Nd),[7] reflecting the smaller coordination number and negative charge of the complexes. As observed with the cyclopentadienyl complexes, the Ln−N and Ln−S distances are intermediate between typical σ and donor bond lengths, and the average C(1)−N(1) and C(1)−S(1) bond lengths are intermediate

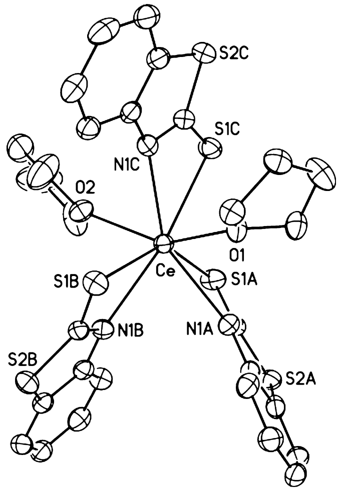

Figure 1. View of $[Ce(SBT)_3(THF)_2]$. The hydrogen atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level.

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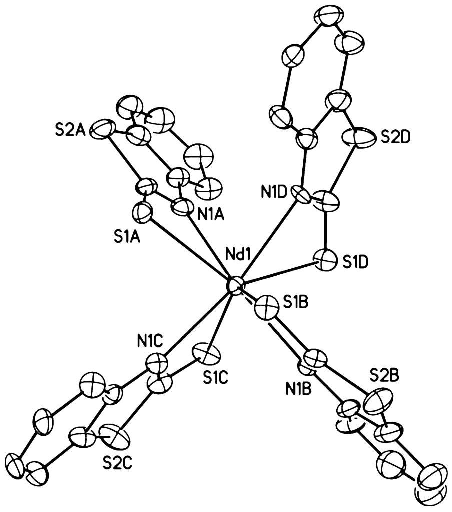

Figure 2. View of one of the two independent anions $[Nd(SBT)_4]^-$. The hydrogen atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 30% probability level.

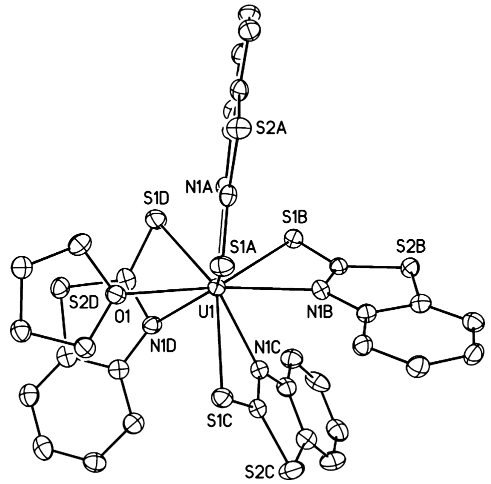

Figure 3. View of one of the two independent molecules of $[U(SBT)_4(THF)]$. The hydrogen atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level.

between single and double bond lengths, reflecting the thionate character of the SBT ligand.

Treatment of $[Ln(BH_4)_3(THF)_3]$ with 4 mol equiv of KSBT, by using the same procedure as for the synthesis of the neutral tris(SBT) complexes, gave yellow (Ln = Ce) or blue (Ln = Nd) powders of $[K(THF)Ln(SBT)_4]$ which are insoluble in THF and were transformed into the soluble pyridine adducts $[K(py)_4Ln(SBT)_4]$. Slow diffusion of pentane into a pyridine solution of $[K(py)_4Nd(SBT)_4]$ in the presence of 15-crown-5 afforded pale blue crystals of $[K(15\text{-crown-}5)_2][Nd(SBT)_4]$. This complex is, after $[Th(SBT)_4]$,[11] $[ML_3][M'(SBT)_4]$ (M = Ni or Co; M′ = Zn or Hg; L = phen or en),[25] and $[NMe_4]_2[Hg(SBT)_4]$,[26] a new example of a tetrakis(SBT) compound, and the first one to have been crystallographically characterized. A view of one of the two independent and quite similar anions $[Nd(SBT)_4]^-$ is presented in Figure 2. The four bidentate SBT ligands form a distorted dodecahedron defined, in anion 1, by the two trapezia N(1A)−S(1A)−S(1B)−N(1B) and N(1C)−S(1C)−S(1D)−N(1D) [rms deviations of 0.249 and 0.218 Å] which intersect at an angle of 89.10(14)°; the equivalent sites A and B of the dodecahedron are occupied by the S and N atoms, respectively. The geometrical parameters of the SBT ligands are identical to those in $[Nd(SBT)_3(THF)_2]$.

The ^1H NMR spectra of the homoleptic lanthanide complexes and their Lewis base adducts indicate that the SBT ligands are chemically equivalent, even at low temperature, and likely undergoing rapid intramolecular exchange in solution.

Lewis Base Adducts of the Homoleptic Uranium Complexes. Reaction of $U(BH_4)_4$ with 4 mol equiv of KSBT in THF at 20 °C readily afforded an orange solution of $[U(SBT)_4(THF)_x]$, and, after filtration and evaporation to dryness, an orange powder which analyses as $[U(SBT)_4(THF)_2]$ was isolated in 96% yield. Slow diffusion of pentane into the THF solution gave light brown crystals of $[U(SBT)_4(THF)]$ suitable for X-ray diffraction. A view of one of the two independent and very similar molecules of $[U(SBT)_4(THF)]$ is shown in Figure 3. The SBT ligands adopt the bidentate ligation mode, and the nine-coordinate environment of the U atom can be seen as a distorted capped square antiprism; the two faces N(1A)−N(1B)−S(1C)−O(1) and N(1C)−N(1D)−S(1B)−S(1D) in molecule 1 [N(1H)−N(1E)−S(1F)−O(2) and N(1F)−N(1G)−S(1G)−S(1E) in molecule 2], coplanar with maximum deviations of 0.206 and 0.148 Å [0.204 and 0.001 Å], form an angle of 8.63(10)° [11.60(10)°], while S(1A) [S(1H)] is in capping position. The U−N and U−S distances in the two independent molecules, which average 2.53(2) and 2.87(3) Å, respectively, can be compared with those of 2.51(4) and 2.84(3) Å in $[U(Cp^*)(SBT)_3]$.

Attempts to prepare the neutral uranium(III) compound $[U(SBT)_3]$ by treatment of $[U\{N(SiMe_3)_2\}_3]$ or $[U(BH_4)_3(THF)_3]$ with HSBT or by reaction of $[UI_3(THF)_3]$ or $[U(BH_4)_3(THF)_3]$ with KSBT were unsuccessful; the sole detectable product was $[U(SBT)_4]$. The latter, formed in about 10–20% yield, could result from oxidation with adventitious traces of air, but it is also plausible that $[U(SBT)_3]$ underwent a ligand and valence redistribution reaction leading to $[U(SBT)_4]$ and an unknown subvalent uranium complex, a behavior which was noticed with the uranium(III) thiolate complexes $[U(SMes^*)_3]$ ($SMes^* = SC_6H_2{}^tBu_3$-2,4,6)[9] and $[\{U(C_5H_4{}^tBu)_2(SPh)\}_2]$.[27] The anionic complex $[U(SBT)_4L]^-$ (L = THF or py) was synthesized by reduction of $[U(SBT)_4(THF)_2]$ with sodium or potassium amalgam; the reaction was not clean, even in the presence of a crown-ether which is essential to avoid the formation of decomposition products, possibly due to the dissociation of $[U(SBT)_4L]^-$ into the unstable $[U(SBT)_3]$ species. Oxidation of $[U(SBT)_4L]^-$ with AgI gave back the uranium(IV) precursor. In one experiment with K(Hg) and 15-crown-5, a few dark brown crystals of $[K(15\text{-crown-}5)_2][U(SBT)_4(py)]$ were obtained; a view of the anion is shown in Figure 4. The uranium atom is in a

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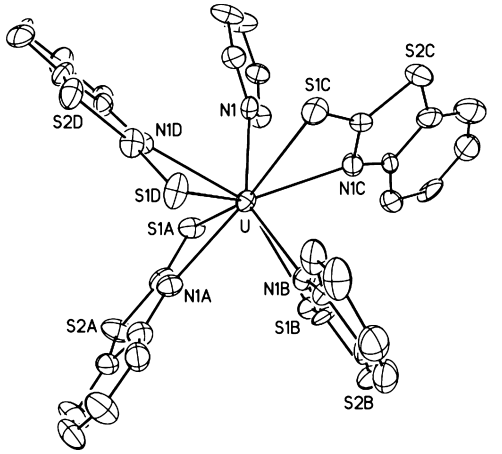

Figure 4. View of the anion $[U(SBT)_4(py)]^-$. The hydrogen atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 30% probability level.

distorted capped square antiprismatic environment, the two square faces S(1A)−S(1B)−N(1C)−N(1) and N(1A)−N(1B)−S(1C)−N(1D) [rms deviations 0.102 and 0.207 Å] forming an angle of 6.3(3)°, and S(1D) being in capping position. The configuration of the anion is distinct from that of the neutral uranium(IV) congener since three SBT ligands are spanning edges linking the two square faces of the antiprism in the former, instead of two in the latter. The U−N(1) and U−S(1) distances are about 0.1 Å larger than in the parent U^{IV} compound, in agreement with the difference between the radii of the U^{4+} and U^{3+} ions;[24] as a consequence, the bite angles of the SBT ligands are smaller, by about 2°, in the uranium(III) complex. The average U−N(1)(SBT) distance of 2.63(2) Å is slightly smaller than the U−N(1)(py) distance of 2.677(11) Å which can be compared with that of 2.665(6) Å in $[U(C_5H_4{}^tBu)_3(py)]$.[28] The mean U−S bond length of 3.00(3) Å is larger than that of 2.720(5) Å in $[U(SMes^*)_3]$, the unique example of a homoleptic thiolate complex of uranium(III),[9] and is slightly larger than that of 2.928(11) Å in the bis(thioimidazolyl)borate compound $[U\{H(Ph)B(tim^{Me})_2\}_2(THF)_3][BPh_4]$ (tim^{Me} = 2-mercapto-1-methylimidazolyl).[29]

It is noteworthy that the uranium(III) anion $[U(SBT)_4(py)]^-$retains a pyridine molecule in its coordination sphere, in contrast to $[Nd(SBT)_4]^-$. This difference cannot be explained by the larger ionic radius of U^{3+} with respect to Nd^{3+} (1.160 versus 1.109 Å for eight coordination)[24] because in the neutral compound $[U(SBT)_4(THF)]$, the THF molecule is bound to the U^{4+} ion which is smaller (0.997 Å) than Nd^{3+}. This better affinity of U^{III} versus Nd^{III} for the pyridyl moiety, which is reminiscent of that observed with the complexes $[UI_2(terpy)_2(py)]^+$ and $[LnI_2(terpy)_2]^+$ (Ln = Ce, Nd),[30] could reflect the relatively greater softness of the trivalent 5f ion. By considering the differences in coordination numbers and ionic radii, one could predict that the U−S and U−N distances in $[U(SBT)_4(py)]^-$ would be 0.1 Å larger than the Nd−S and Nd−N distances in $[Nd(SBT)_4]^-$. This is indeed the case for the U−N and Nd−N distances which average 2.63(2) and 2.540(11) Å, respectively, whereas the U−S distances seem to be 0.04 Å shorter than those expected from a purely ionic bonding model. This variation, if significant, could also be related to the softer character of the actinide ion.

Conclusion

The first homoleptic lanthanide(III) and uranium(IV) SBT complexes and/or their Lewis base adducts were prepared from the borohydride precursors. The crystal structures show the bidentate ligation mode and the thionate character of the SBT ligand. Despite its thermal instability, the anionic uranium(III) derivative $[K(15\text{-crown-}5)_2][U(SBT)_4(py)]$, obtained by reduction of the parent uranium(IV) complex, was characterized by its crystal structure which, by comparison with that of the neodymium analogue $[K(15\text{-crown-}5)_2][Nd(SBT)_4]$, reflects the greater softness of the trivalent actinide ion.

Supporting Information Available: Tables of crystal data, atomic positions and displacement parameters, anisotropic displacement parameters, bond lengths and bond angles in CIF format (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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