Synthesis, Characterization, and X-ray Structure of the Uranium Thiolate Complex $U(S\text{-}2,6\text{-}Me_2C_6H_3)[N(SiMe_3)_2]_3$

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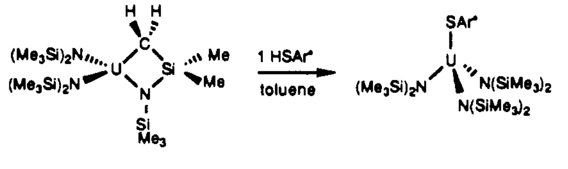
We previously reported[2] that metallacyclic actinide complexes $[\{(Me_3Si)_2N\}_2An(CH_2SiMe_2NSiMe_3)]$ (An = Th, U)[3] react with 4 equiv of 2,6-disubstituted phenols $HO\text{-}2,6\text{-}R_2C_6H_3$ (R = H, Me, i-Pr) to produce homoleptic actinide *tetra*aryloxide complexes $An(OAr)_4$. The reaction was shown to proceed in a stepwise manner whereby the first equivalent of added phenol protonates the metal–carbon bond to form a monoaryloxide species $An(OAr)[N(SiMe_3)_2]_3$, and subsequent protonation steps generate the *bis*-, *tris*-, and *tetrakis*(aryloxide) complexes $An(OAr)_2[N(SiMe_3)_2]_2$, $An(OAr)_3[N(SiMe_3)_2]$, and $An(OAr)_4$, respectively. In the case of the thorium metallacycle, reactions employing sterically demanding 2,6-di-*tert*-butylphenol lead only to the tris(aryloxide) species $Th(O\text{-}2,6\text{-}t\text{-}Bu_2C_6H_3)_3[N(SiMe_3)_2]$ even after prolonged reflux (36 h) in toluene. Due to the paucity of actinide thiolate complexes reported to date,[4–6] it was of interest to examine the corresponding reactions between the actinide metallacycle $[\{(Me_3Si)_2N\}_2An(CH_2SiMe_2NSiMe_3)]$ and substituted arenethiol reagents in an attempt to prepare homoleptic thiolate complexes $An(SAr)_4$.

In contrast to the relatively clean products obtained by reaction with disubstituted phenols, treatment of the uranium metallacycle $[\{(Me_3Si)_2N\}_2U(CH_2SiMe_2NSiMe_3)]$ with 4 equiv of 2,6-disubstituted arenethiol yielded highly insoluble, intractable products. The nature of these products is still under investigation although we believe that they could be uranium sulfides. We have determined however, that treatment of a toluene solution of the uranium metallacycle $[\{(Me_3Si)_2N\}_2U(CH_2SiMe_2NSiMe_3)]$ with *1* equiv of 2,6-dimethylthiophenol at room temperature, followed by crystallization from 1:1 toluene/hexane, gives the brown crystalline monothiolate $U(S\text{-}2,6\text{-}Me_2C_6H_3)[N(SiMe_3)_2]_3$ (**1**) in good yield as outlined in eq 1. Subsequent reaction between $U(S\text{-}2,6\text{-}Me_2C_6H_3)[N(SiMe_3)_2]_3$ and additional equivalents of arenethiol gives intractable products, even at low temperature. Four-coordinate early actinide complexes are relatively rare, and thus we describe here the X-ray structure of the monothiolate $U(S\text{-}2,6\text{-}Me_2C_6H_3)[N(SiMe_3)_2]_3$ and some of its physical and spectroscopic properties.



(1)

Table I. Summary of Crystallographic Data for $U(S\text{-}2,6\text{-}Me_2C_6H_3)[N(SiMe_3)_2]_3$

empirical formula	$C_{26}H_{63}N_3SSi_6U$
color and habit	clear amber crystal in a capillary
cryst size, mm	0.2 × 0.3 × 0.2
space group	*Pbca*
unit cell dimens	
a, Å	19.614(4)
b, Å	18.607(4)
c, Å	21.510(4)
vol, $Å^3$	7850(3)
Z	8
fw	856.4
D_{calc}, g cm^{-3}	1.449
abs coeff, mm^{-1}	4.171
F(000)	3456
λ(Mo Kα Radiation), Å	0.710 69
temp, °C	−40
no. of measd reflcns	5897
no. of unique reflcns	5093 (R_{int} = 5.29%)
no. of obsd reflcns	3206 ($F > 3.0\sigma(F)$)
R	0.045
R_w	0.064
goodness-of-fit	0.65

Experimental Section

General Procedures and Techniques. All manipulations were carried out under an inert atmosphere of oxygen-free UHP grade argon using standard Schlenk techniques, or under oxygen-free helium in a Vacuum Atmospheres glovebox. $[\{(Me_3Si)_2N\}_2U(CH_2SiMe_2NSiMe_3)]$[3c] was prepared as described previously; 2,6-dimethylthiophenol was purchased from Aldrich and degassed prior to use. Solvents were degassed and distilled from Na/K alloy under nitrogen. Benzene-d_6 and toluene-d_8 were degassed, dried over Na/K alloy, and then trap-to-trap distilled before use. Solvents were taken into the glovebox and a small amount tested with a solution of sodium benzophenone in THF. Solvents that failed to maintain a purple coloration from this test were not used.

^1H NMR spectra were recorded at 22 °C on a Bruker WM 300 spectrometer. All ^1H NMR chemical shifts are reported in ppm relative to the ^1H impurity in benzene-d_6 or toluene-d_8 set at δ 7.15 or 2.09, respectively. Infrared spectra were recorded on a Perkin-Elmer 1500 spectrophotometer interfaced with a Model 1502 central processor. Elemental analyses were performed on a Perkin-Elmer 2400 CHN analyzer. Elemental analysis samples were prepared and sealed in tin capsules in the glovebox prior to combustion.

Synthesis of $U(S\text{-}2,6\text{-}Me_2C_6H_3)[N(SiMe_3)_2]_3$. A 2.00-g (2.78-mmol) sample of $[\{(Me_3Si)_2N\}_2U(CH_2SiMe_2NSiMe_3)]$ was dissolved in 75 mL of toluene and a solution of 0.39 g (2.82 mmol) of 2,6-dimethylthiophenol in toluene (20 mL) was added dropwise with stirring over a period of 10 min. A small amount of flocculent yellow precipitate was formed as the thiol was added. The resulting solution was stirred at room temperature for 2 h before being vacuum-filtered through Celite on a medium-porosity frit. The Celite pad and frit were washed with toluene until the filtrate was colorless. The toluene was then removed in vacuo from the filtrate to leave an orange/brown solid residue. Recrystallization of the residue from 1:1 hexane/toluene (20 mL) gave 2.11 g (88 %) of **1** as orange-brown needles. Anal. Calcd for $C_{26}H_{63}N_3SSi_6U$: C, 36.46; H, 7.41; N, 4.91. Found: C, 36.55; H, 6.32; N, 4.48. ^1H NMR (300 MHz, 22 °C, C_6D_6): δ 0.86 (m, 3H, $C_6H_3Me_2$), −2.80 [br s, 54H, $N(SiMe_3)_2$], −11.17 (s, 6H, $C_6H_3Me_2$). IR (Nujol, cm^{-1}): 1254 (s), 1052 (m), 882 (s, sh), 848 (s), 774 (s), 762 (s), 658 (m), 616 (s), 590 (m, sh).

Structural Determination. Crystal data and collection and processing parameters are given in Table I. X-ray quality crystals of **1** were grown from a concentrated toluene solution at −40 °C. A crystal measuring 0.20 × 0.30 × 0.20 mm was coated in Nujol and mounted on a glass fiber under an argon purge. The fiber was then placed on the goniometer head

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Table II. Fractional Coordinates and Equivalent Isotropic Displacement Coefficients[a] for $U(S\text{-}2,6\text{-}Me_2C_6H_3)[N(SiMe_3)_2]_3$

	10^4x	10^4y	10^4z	10^4U(eq), Å^2
U(1)	2123(1)	1523(1)	1695(1)	203(2)
S(1)	1851(2)	2931(2)	1853(2)	289(11)
Si(1)	489(2)	1169(2)	1359(2)	292(12)
Si(2)	1386(2)	846(2)	274(2)	303(12)
Si(3)	3721(2)	2241(2)	1034(2)	321(12)
Si(4)	3533(2)	683(2)	1304(2)	301(12)
Si(5)	2549(2)	1712(2)	3224(2)	302(12)
Si(6)	1942(2)	282(2)	2963(2)	350(13)
N(1)	1308(5)	1150(5)	1039(4)	232(32)
N(2)	3190(5)	1557(6)	1312(4)	270(34)
N(3)	2217(5)	1117(6)	2666(4)	262(34)
C(1)	1094(6)	3248(6)	1462(7)	327(45)
C(2)	552(7)	3477(7)	1841(6)	368(48)
C(3)	−28(7)	3742(8)	1504(8)	430(56)
C(4)	−40(8)	3784(9)	894(9)	593(63)
C(5)	510(9)	3589(7)	532(8)	531(60)
C(6)	1100(8)	3312(6)	818(6)	373(50)
C(7)	556(7)	3458(7)	2529(7)	426(55)
C(8)	1690(7)	3111(8)	420(6)	415(52)
C(9)	−100(7)	1809(8)	977(7)	453(55)
C(10)	44(7)	290(7)	1347(6)	390(51)
C(11)	574(7)	1496(7)	2192(6)	354(47)
C(12)	2247(7)	1052(8)	−56(6)	393(51)
C(13)	1267(8)	−155(8)	224(7)	520(58)
C(14)	765(8)	1276(9)	−258(7)	529(60)
C(15)	3587(8)	2368(8)	189(7)	556(62)
C(16)	4645(6)	2062(8)	1185(7)	515(57)
C(17)	3603(8)	3131(7)	1390(7)	490(54)
C(18)	2807(6)	26(7)	1382(7)	393(49)
C(19)	3975(7)	450(8)	568(6)	509(56)
C(20)	4098(7)	499(8)	1986(6)	408(51)
C(21)	1867(7)	2280(7)	3590(7)	404(51)
C(22)	3043(7)	1250(8)	3858(6)	384(50)
C(23)	3164(7)	2326(7)	2850(6)	399(49)
C(24)	1411(7)	372(8)	3679(6)	481(55)
C(25)	2663(8)	−344(8)	3138(7)	516(56)
C(26)	1384(7)	−188(7)	2393(6)	435(53)

[a] $U(\text{eq}) = {}^1/_3[U_{11} + U_{22} + U_{33}]$.

of an Enraf-Nonius CAD-4 diffractometer in a 233 K nitrogen cold stream. Graphite-monochromated Mo Kα radiation was used. Unit cell parameters were determined from the least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 24 accurately-centered reflections. Examination of the systematic absences uniquely identified the space group as *Pbca*. Two reflections were chosen as intensity standards and measured every 150 reflections. Data were collected by 2θ–θ scans.

Equivalent reflections were merged and systematically absent reflections were rejected. The structure was solved by routine Patterson and Fourier methods. After inclusion of anisotropic thermal parameters for all non-hydrogen atoms and geometrical generation of hydrogen atoms which were constrained to "ride" upon the appropriate carbon atoms, final refinement using 3206 unique observed ($F > 3\sigma(F)$) reflections converged at $R = 0.0451$, $R_w = 0.0638$ (where $w = 1/[\sigma^2(F)^2 + 0.0084F^2]$). All calculations were performed using the SHELXTL PLUS suite of computer programs (Siemens Analytical X-ray Instr., Inc. 1990). A correction for absorption was applied.[7] Atomic positional parameters are given in Table II.

Results and Discussion

In the solid state, $U(S\text{-}2,6\text{-}Me_2C_6H_3)[N(SiMe_3)_2]_3$ is monomeric, with three amido nitrogen atoms, and the sulfur atom of the thiolate ligand coordinated to the uranium atom in an approximately tetrahedral fashion. A view of the molecule is shown in Figure 1, while selected bond lengths and angles are given in Table III. The uranium–sulfur distance of 2.696(3) Å may be compared with that of 2.680(6) Å in $U(S\text{-}i\text{-}Pr)_2(HBPz_3)_2$,[5] 2.60(1) Å in $[(C_5H_4Me)_3U]_2S$,[8] and 2.885 Å (average) and 2.816 Å (average) in the "A" and "B" dodecahedral sites of $[Li(DME)]_4[U(SCH_2CH_2S)_4]$.[4] The U(1)–S(1)–C(1) angle of 114.9(4)° is similar to the U–S–C angle of 115(1)° and the Th–S–C angle of 108.3(5)° found in the solid-state structures of $U(S\text{-}i\text{-}Pr)_2(HBPz_3)_2$,[5] and $Th(S\text{-}n\text{-}Pr)_2(C_5Me_5)_2$.[6] These angles are relatively acute when compared with An–O–C angles in alkoxide analogues which have bond angles that span between 160 and 180°.[9] The U–O–C angle is 158.6(8)° in the related aryloxide complex $U(O\text{-}2,6\text{-}Bu^t{}_2C_6H_3)[N(SiMe_3)_2]_3$.[2] The silylamide ligands are distorted somewhat away from one another and toward the thiophenoxide moiety (the average N–U–S angle being 102.9°). Angles between nitrogen atoms span a relatively wide range from 106.1(3)° for N(2)–U(1)–N(3) to 122.9(3) for N(1)–U(1)–N(3). The distortions observed within the three silylamide ligands are such that one trimethylsilyl group of each silylamide ligand approaches the metal center more closely than the other. The most pronounced distortion occurs within the silylamide ligand containing N(2), Si(3), and Si(4), for which we observe a relatively small U(1)–N(2)–Si(4) angle of 109.5(5)°, while the U(1)–N(2)–Si(3) angle is opened out to 134.4(6)°. This distortion manifests itself in a notably close U(1)- -C(18) contact of 3.158 Å. The other two silylamide ligands show similar, though somewhat smaller, distortions resulting in U- -C distances of 3.233 and 3.539 Å for C(11) and C(23), respectively. These U- -C distances may be compared with those of 3.09(2) Å in the uranium(III) alkyl

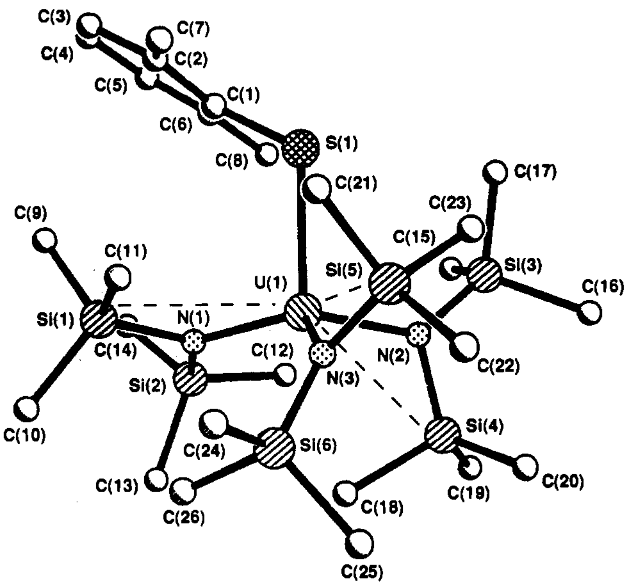

Figure 1. Ball-and-stick drawing of the solid-state molecular structure of $U(S\text{-}2,6\text{-}Me_2C_6H_3)[N(SiMe_3)_2]_3$ giving the atom numbering scheme used in the tables.

Table III. Selected Bond Distances (Å) and Bond Angles (deg) for the $U(S\text{-}2,6\text{-}Me_2C_6H_3)[N(SiMe_3)_2]_3$ Molecule

U(1)–S(1)	2.696(3)	U(1)–Si(1)	3.352(4)
U(1)–Si(4)	3.287(4)	U(1)–Si(5)	3.410(4)
U(1)–N(1)	2.243(9)	U(1)–N(2)	2.250(10)
U(1)–N(3)	2.228(9)	S(1)–C(1)	1.807(13)
Si(1)–N(1)	1.749(10)	Si(4)–N(2)	1.760(11)
Si(2)–N(1)	1.747(10)	Si(5)–N(3)	1.757(10)
Si(3)–N(2)	1.749(11)	Si(6)–N(3)	1.765(11)
S(1)–U(1)–N(1)	103.8(3)	S(1)–U(1)–N(3)	103.1(3)
S(1)–U(1)–N(2)	101.7(3)	N(1)–U(1)–N(3)	122.9(3)
N(1)–U(1)–N(2)	116.2(3)	U(1)–N(2)–Si(3)	134.4(6)
U(1)–S(1)–C(1)	114.9(4)	U(1)–N(3)–Si(5)	117.2(5)
U(1)–N(1)–Si(2)	129.1(5)	Si(5)–N(3)–Si(6)	114.9(5)
N(2)–U(1)–N(3)	106.1(3)	U(1)–N(1)–Si(1)	113.6(5)
Si(3)–N(2)–Si(4)	116.2(6)	Si(1)–N(1)–Si(2)	117.3(5)
U(1)–N(3)–Si(6)	127.8(5)	U(1)–N(2)–Si(4)	109.5(5)

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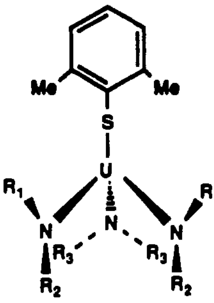
$U[CH(SiMe_3)_2]_3$, in which a γ-agostic interaction was proposed.[10] The average U–N distance of 2.240(12) Å in **1** is very close to those found previously for terminal, tetravalent U–N bond lengths in $[U(NEt_2)_4]_2$, $[U(MeNCH_2CH_2NMe)_2]_3$, $[U(MeNCH_2CH_2NMe)_2]_4$, $U(NPh_2)_4$, $HU[N(SiMe_3)_2]_3$, and $(Et_2N)U(O\text{-}2,6\text{-}t\text{-}Bu_2C_6H_3)_3$ which are 2.22,[11] 2.21,[12] 2.27,[13] 2.24,[14] 2.24,[15] and 2.16 Å,[16] respectively.

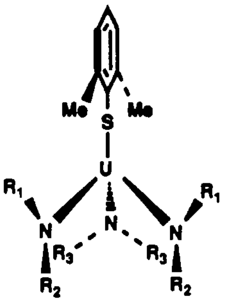
There are now a number of examples in the literature of lanthanide and actinide complexes for which γ-agostic interactions have been proposed between the metal center and a trimethylsilyl group of an amide $[N(SiMe_3)_2]$ or alkyl $[CH(SiMe_3)_2]$ ligand.[17-19] Similar γ-agostic, or β-methyl, interactions have recently been the subject of a detailed study by Schaverian.[20] Silicon atoms Si(1), Si(4), and Si(5) are closest to the metal, with distances of U(1)–Si(1) = 3.352(4) Å, U(1)–Si(4) = 3.287(4) Å, and U(1)–Si(5) = 3.410(4) Å.

The previously reported structures of $HU[N(SiMe_3)_2]_3$,[15] $BH_4Th[N(SiMe_3)_2]_3$,[21] and $U[CH(SiMe_3)_2]_3$[10] all possess crystallographic 3-fold symmetry relating the trimethylsilyl-containing ligands. In the structure of **1**, however, the silylamide ligand below the arenethiolate ring [i.e. that containing N(1)] is twisted noticeably when compared to the other two silylamide ligands, such that the plane comprising N(1), Si(1), and Si(2) is almost parallel to the arene ring.

Room-temperature ^1H NMR data show a single resonance at δ −2.80 for the six trimethylsilyl groups, indicating that the asymmetry seen in the solid-state structure is either lost in solution or averaged out by rapid fluxional behavior. When the temperature is lowered, both the trimethylsilyl and thiophenoxide methyl resonances broaden and disappear into the baseline at 220 K. Further cooling down to 155 K reveals the emergence of three new silylamide signals. This variable-temperature behavior is similar to that seen in $U(O\text{-}2,6\text{-}t\text{-}Bu_2C_6H_3)[N(SiMe_3)_2]_3$[2] which was rationalized based upon structures possessing a mirror plane of symmetry. Two plausible structures are shown in **A** and **B**, which represent schematic views of **1** looking down the mirror plane containing C(ipso)–S–U–N. Note that either **A** or **B** would give rise to three types of silylamide ligands in a 1:1:1 ratio as indicated (R_1, R_2, R_3) in the drawing. Restricted rotation about the U–N bonds of the two silylamide ligands related by the plane of symmetry would result in two different $SiMe_3$ signals for groups proximal and distal to the aryloxide ligand, and these groups are labeled as R_1 and R_2 in the drawings above. The same plane of symmetry equivalences the $SiMe_3$ groups of the third silylamide ligand.



A



B

The structure illustrated in **A** most closely approximates that observed in the solid-state structure of **1** (Figure 1). Structures **A** and **B** are both consistent with the low-temperature ^1H NMR spectra, assuming rapid rotation about the U–S or S–C bonds in **B** and restricted rotation about the U–N bonds. At room temperature, rapid rotation about the U–N bonds would equivalence all $SiMe_3$ groups, producing the observed coalescence of ^1H NMR resonances.

In summary, we have shown that a relatively rare example of a four-coordinate, early actinide thiolate complex, $U(S\text{-}2,6\text{-}Me_2C_6H_3)[N(SiMe_3)_2]_3$, can be prepared by protonation of the uranium–carbon bond of metallacyclic $[\{(Me_3Si)_2N\}_2U(CH_2SiMe_2NSiMe_3)]$. The formal protonation of the U–C bond to form $U(S\text{-}2,6\text{-}Me_2C_6H_3)[N(SiMe_3)_2]_3$ is directly comparable to the reactions with alcohols or substituted phenols to form $U(OR)[N(SiMe_3)_2]_3$ complexes. In contrast, reaction between $U(S\text{-}2,6\text{-}Me_2C_6H_3)[N(SiMe_3)_2]_3$ and further equivalents of added thiophenol does not lead to the isolation of additional substitution products as seen in the corresponding alkoxide chemistry. In contrast to the extensive coordination chemistry of actinide elements with hard oxygen donor ligands, the corresponding chemistry with sulfur donor ligands is exceedingly limited.[4-6] While the synthesis of homoleptic thiolates $U(SEt)_4$ and $U(S\text{-}t\text{-}Bu)_4$ were reported by Gilman in the mid 1950s,[22] $U(SCH_2CH_2S)_4^{4-}$ appears to be the only homoleptic uranium thiolate complex that has been structurally characterized.[4] Alternate routes to the preparation and characterization of $U(SAr)_4$ compounds are being examined.

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Supplementary Material Available: Tables listing a complete summary of crystallographic data, bond lengths and angles, and anisotropic thermal parameters for $U(S\text{-}2,6\text{-}Me_2C_6H_3)[N(SiMe_3)_2]_3$ (4 pages). Ordering information is given on any current masthead page. Crystallographic structure factor tables are available from the authors upon request.

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