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Synthesis and Crystal Structure of the Homoleptic Uranium(IV) Thiolates $[(thf)_3Na(\mu\text{-}SR)_3U(\mu\text{-}SR)_3Na(thf)_3]$ (thf = tetrahydrofuran; R = Bu^t or Ph)†

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The uranium(IV) hexathiolate complexes $[(thf)_3Na(\mu\text{-}SR)_3U(\mu\text{-}SR)_3Na(thf)_3]$ (thf = tetrahydrofuran; R = Bu^n, Pr^i, Bu^t or Ph) were prepared by treatment of UCl_4 or $U(BH_4)_4$ with the corresponding NaSR reagent. The crystal structures of the *tert*-butyl and phenyl derivatives have been determined. Reaction of $U(SBu^n)_4$ with NaSBu^n gave the anion $[U(SBu^n)_6]^{2-}$ which, by protonation with NEt_3HBPh_4, was transformed back into $U(SBu^n)_4$.

In contrast to the great variety of organosulfur d-transition-metal complexes, derivatives of the lanthanides and actinides with S-donor ligands are rather limited,[1–6] even though the bonding between these hard metals and soft ligands is of particular interest. The first homoleptic thiolate compounds of an f element, $U(SEt)_4$ and $U(SBu^n)_4$, were obtained in 1956 by Gilman and co-workers,[5] by treatment of $U(NEt_2)_4$ with the corresponding thiol. The discovery of these pyrophoric powders did not give rise to further investigations and such actinide thiolate complexes were practically ignored until 1990, when Tatsumi *et al.*[6] prepared the first homoleptic dithiolate complex of an f element, $[Li(dme)]_4[U(SCH_2CH_2S)_4]$, isolated from the reaction of UCl_4 with $Li_2SCH_2CH_2S$ in 1,2-dimethoxyethane (dme). We found that reaction of UCl_4 or $U(BH_4)_4$ with NaSR reagents in tetrahydrofuran (thf) gave the hexathiolato complexes $[Na(thf)_3]_2[U(SR)_6]$ and here we describe the synthesis and crystal structure of two of them, where R = Bu^t and Ph.

Results and Discussion

Synthesis.—In order to synthesise the neutral complex $U(SBu^t)_4$ we first tried the reaction of $U(BH_4)_4$ with NaSBu^t (4 equivalents) in tetrahydrofuran. Instead of the green colour expected for the product, we observed a red solution which, after concentration, deposited red crystals of $[Na(thf)_3]_2[U(SBu^t)_6]$ **1**, in 30% yield. The elemental analyses (C, H, S) of a sample of **1** were in agreement with its formula; however the bright crystals became progressively opaque by drying under vacuum, suggesting a desolvation reaction. The NMR spectra of the complex were not very informative: a single resonance corresponding to equivalent SBu^t groups was visible near δ 2.6, at any temperature between 30 and 50 °C; the signal was not affected after addition of 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane) to the solution. For the bright crystals in $[^2H_5]$pyridine the intensities of the signals corresponding to the thf and SBu^t ligands were in the ratio 24:24:54 (6 thf and 6 SBu^t), and after **1** was dried under vacuum (10^{-2} mmHg, 10 h) these proportions were 8:8:54 (2 thf and 6 Bu^t). The structure of **1** could be unambiguously determined by a single-crystal X-ray diffraction analysis (see below).

With the correct molar ratio of 6 equivalents of NaSBu^t to 1 equivalent of UCl_4 or $U(BH_4)_4$, the yield of compound **1** (crystals) was improved to 52%. Formation of the $[Na(thf)_3]_2[U(SR)_6]$ complexes, by using a variety of NaSR reagents (R = Bu^n, Pr^i, Bu^t or Ph), seemed to be general but, as for **1**, the red products could not be confidently identified by their NMR spectra or their elemental analyses (after drying under vacuum, a sample of the phenyl derivative analysed for $[Na(thf)]_2[U(SPh)_6]$, showing the same loss of thf as for **1**); in the case of R = Bu^t and Ph, the crystal structures were determined (see below). Reactions of UCl_4 with 4 equivalents of NaSPr^i and NaSPh also gave immediately the corresponding anions $[U(SR)_6]^{2-}$ but with NaSBu^n the green neutral complex $U(SBu^n)_4$ was obtained.

Treatment of $[Na(thf)_3]_2[U(SBu^n)_6]$ with NEt_3HBPh_4 (2 equivalents) in tetrahydrofuran afforded a green precipitate of $U(SBu^n)_4$, identical to that prepared by the method of Gilman and co-workers.[5] Not surprisingly, reaction of the neutral compound $U(SBu^n)_4$ with 2 equivalents of NaSBu^n gave the anion $[U(SBu^n)_6]^{2-}$ (NMR experiments).

Comparison between Thiolate and Alkoxide Compounds of the f Elements.—The reactions of UCl_4 with 4 equivalents of alkali-metal thiolate or alkoxide reagents are quite different since the former readily afforded the anions $[U(SR)_6]^{2-}$ or $[U(SCH_2CH_2S)_4]^{4-}$ [5] whereas the latter led to the formation of the neutral tetraalkoxide compounds $[U(OR)_4]$.[7] However, it should be noted that $[KU_2(OBu^t)_9]$[8] was prepared by treatment of UCl_4 with 4.5 equivalents of KOBu^t and that reaction of uranium tetrachloride with 6 equivalents of LiOMe gave presumably $[Li_2U(OMe)_6]$, which was used as intermediate in the synthesis of $[U(OMe)_6]$.[9] It is also interesting that reaction of $[(C_5R_5)_2Lu(\mu\text{-}Me)_2Li(thf)_2]$ (R = H or Me) with 2 equivalents of Bu^{t}OH or Bu^{t}SH afforded respectively $[Lu(C_5R_5)_2(OBu^t)(thf)]$ and $[(C_5R_5)_2Lu(\mu\text{-}SBu^t)_2Li(thf)_2]$.[4] These features should be accounted for by the distinct electronic effects of the alkoxide and thiolate ligands; it seems that a [U]–SR entity, being less electron rich than its [U]–OR analogue, would be inclined to increase the charge density around the metal. That a thiolate ligand is less electron donating than an alkoxide group was indicated by the reduction potentials of the

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Non-SI unit employed: mmHg ≈ 133 Pa.

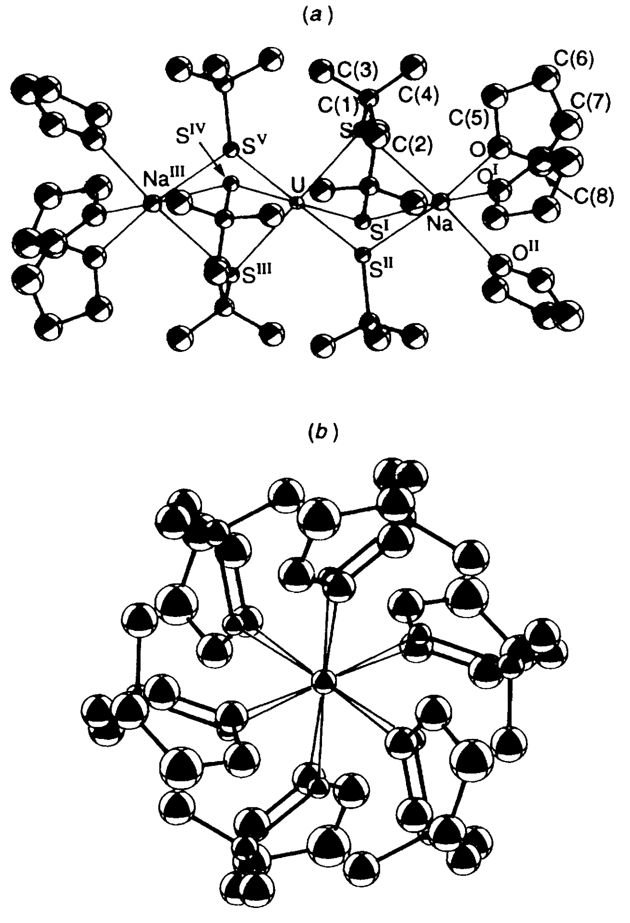

Fig. 1 (a) Perspective view of $[\mathrm{Na(thf)_3}]_2[\mathrm{U(SBu^t)_6}]$; for explanation of Roman superscripts see Table 1. (b) View along the Na–U–Na ternary axis

Table 1 Selected bond distances (Å) and angles (°) with estimated standard deviations (e.s.d.s)

$[\mathrm{Na(thf)_3}]_2[\mathrm{U(SBu^t)_6}]$		$[\mathrm{Na(thf)_3}]_2[\mathrm{U(SPh)_6}]$	
U–S	2.750(9)	U–S	2.717(3)
Na–S	2.965(8)	Na–S	3.060(3)
Na–O	2.49(3)	Na–O	2.35(1)
S–C(1)	1.88(3)	S–C(1)	1.79(1)
U–S–C(1)	125(1)	U–S–C(1)	112.1(3)
U–S–Na	85.7(3)	U–S–Na	88.26(9)
S–U–S$^{\mathrm{I}}$	82.4(3)	S–U–S$^{\mathrm{II}}$	82.18(9)
S–Na–O$^{\mathrm{II}}$	173.5(9)	S–Na–O	161.5(3)
S–Na–O	98.2(7)	S–Na–O$^{\mathrm{I}}$	90.3(3)
S–Na–O$^{\mathrm{I}}$	103.3(7)	S–Na–O$^{\mathrm{II}}$	105.5(3)
O–Na–O$^{\mathrm{I}}$	83.2(9)	O–Na–O$^{\mathrm{II}}$	92.6(4)

Symmetry codes: I *z*, *x*, *y*; II *y*, *z*, *x*; III, −*x*, −*y*, −*z*; IV −*z*, −*x*, −*y*; V, −*y*, −*z*, −*x*.

compounds $[\mathrm{U(C_5H_5)_3(OPr^i)}]$ and $[\mathrm{U(C_5H_5)_3(SPr^i)}]$ which are respectively −2.38 and −2.03 V (*vs* ferrocene–ferrocenium).[10] On the other hand, by comparing the structural parameters of the bis(alkanethiolate) complex $[\mathrm{Th(C_5Me_5)_2(SPr^i)_2}]$ with those of alkoxide analogues, it has been suggested that actinide–thiolate bonding involves less ligand-to-metal π donation that does actinide–alkoxide bonding.[3] In this context, also of interest is the unique twist-boat conformation of the $\mathrm{MS_5}$ ring in the polysulfide compound $[\mathrm{Th(C_5Me_5)_2(S_5)}]$, due to coordination of the two β-sulfur atoms to the Lewis acidic thorium(IV) centre.[11]

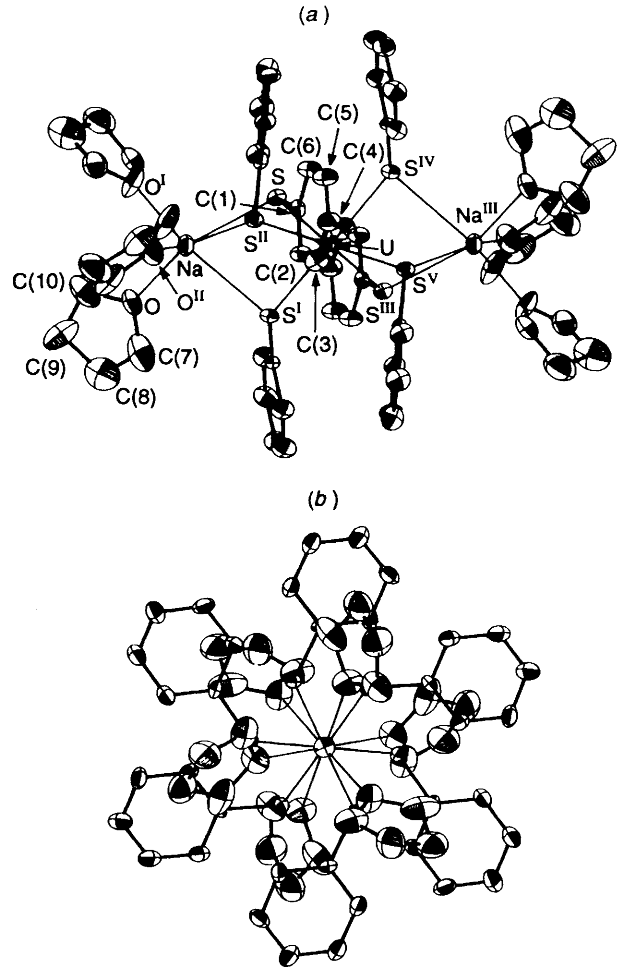

Fig. 2 (a) Perspective view of $[\mathrm{Na(thf)_3}]_2[\mathrm{U(SPh)_6}]$; for explanation of Roman superscripts see Table 1. (b) View along the Na–U–Na ternary axis.

Crystal Structures of $[\mathrm{(thf)_3Na(\mu\text{-}SR)_3U(\mu\text{-}SR)_3Na(thf)_3}]$ (R = $\mathrm{Bu^t}$ *or* Ph).—The ORTEP drawings[12] of the complexes are shown in Figs. 1 (R = $\mathrm{Bu^t}$) and 2 (R = Ph); selected bond distances and angles are in Table 1. The two structures, which are quite similar, reveal that the uranium and sodium atoms lie on a three-fold axis and, in addition, the uranium atom is on an inversion centre. The U and Na atoms are joined by three sulfur bridge bonds and the six equivalent S atoms form a slightly distorted octahedron around the uranium atom. Each sodium is also in an octahedral environment, with three tetrahydrofuran and three bridging thiolate ligands in relative *trans* positions. If the S–U–S bond angles and U–S bond distances are very similar in the two compounds [S–U–S 82.4(3) and 82.18(9)°, U–S 2.750(9) and 2.717(3) Å for R = $\mathrm{Bu^t}$ and Ph respectively], the O–Na–O bond angle is more acute and the Na–O bond length is abnormally long in the *tert*-butyl derivative [O–Na–O 83.2(9) and 92.6(4)°, Na–O 2.49(3) and 2.35(1) Å for R = $\mathrm{Bu^t}$ and Ph respectively]. These distinct structural parameters certainly reflect the steric repulsion between the thf ligands and the bulky $\mathrm{Bu^t}$ groups. The U–S bond length is 0.1 Å shorter than in the anion $[\mathrm{U(SCH_2CH_2S)_4}]^{2-}$ [mean U–S 2.85(5) Å][5] and is similar to that determined in $[\mathrm{U\{HB(pz)_3\}_2(SPr^i)_2}]$ [2.680(6) Å, pz = pyrazolyl][2] these values fall in the range of known U–S distances which vary from 2.60 to 2.95 Å.[13] In the thorium compounds $[\mathrm{Th(C_5Me_5)_2(SPr^i)_2}]$[3] and $[\mathrm{U(C_5Me_5)_2(S_5)}]$,[11] the Th–S bond distances are 2.718(3) and 2.768(4) Å respectively.

Anionic metal thiolates, which are commonly prepared by reaction of metal halides with NaSR reagents, are generally characterized as their $\mathrm{NR_4}^+$ or $\mathrm{PPh_4}^+$ salts.[14] The co-

Table 2 Crystallographic data and experimental details*

	$[Na(thf)_3]_2[U(SBu^t)_6]$	$[Na(thf)_3]_2[U(SPh)_6]$
M	962.30	1371.68
Crystals dimensions (mm)	0.40 × 0.20 × 0.25	0.30 × 0.30 × 0.20
Colour	Red	Red
Crystal system	Cubic	Rhombohedral
Space group	$Pa\bar{3}$	$R\bar{3}$
a/Å	18.840(8)	12.904(5)
α/°	—	67.23(2)
U/Å^3	6687(8)	1754.3(9)
Z	4	1
D_c/g cm^{-3}	1.243	1.298
μ(Mo-Kα)/cm^{-1}	25.289	24.165
$F(000)$	3896	696
Range abs. trans.	0.640–1.451	0.700–1.239
Range h, k, l	0–18	0–12
Reflections collected:		
total	3615	1867
unique	1052	1093
with $I > 3\sigma(I)$	319	1023
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	0.042	0.039
$R' = [\Sigma w\|\|F_o\| - \|F_c\|\|^2/\Sigma w(\|F_o\|)^2]^{\frac{1}{2}}$	0.053	0.054

* Details in common: θ limits 1–20°; scan type ω–2θ; scan width 0.8 + 0.35 tan θ; maximum residual electron density < 1 e Å^{-3}; unit weighting scheme employed.

ordination of the sodium ion in the compounds $[Na(thf)_3]_2[U(SR)_6]$ is, to our knowledge, unprecedented; the Na–S bond distances [2.965(8) and 3.060(3) Å for R = Bu^t and Ph respectively] are very close to that found in [Na(18-crown-6)][W(CO)$_5$(SH)] [3.014(9) Å].[15] Such linear trinuclear structures with six-co-ordinated metal centres are not common but have been encountered in the complexes $[U_3(MeNCH_2CH_2NMe)_6]$[16] and $[Co_3(OCH_2CH_2NH_2)_6]^{2+}$;[17] in these compounds, the three metal atoms have a trigonal-prismatic environment. A similar structure has been proposed for the cation $[Co_3(SCH_2CH_2NH_2)_6]^{3+}$.[18] Finally, we note that the crystal structure of 1 is exceptional since, to our knowledge, only one other molecular actinide complex, $[NEt_4]$-$[Th(NCS)_8]$, was found to crystallize in a cubic system.[19]

Experimental

All preparations and reactions were carried out under argon (< 5 ppm oxygen or water) using standard Schlenk-vessel and vacuum-line techniques or in a glove-box. Solvents were thoroughly dried and deoxygenated by standard methods and distilled immediately before use. Deuteriated solvents were dried over Na–K alloy.

Elemental analyses were performed by Analytische Laboratorien at Engelskirchen (Germany). The ^{1}H NMR spectra were recorded on a Bruker WP 60 (FT) instrument and were referenced internally using the residual protio solvent resonances relative to tetramethylsilane (δ 0). The commercial thiols (Aldrich and Janssen) were dried over molecular sieves. The NaSR reagents were obtained as white powders after the reaction of sodium and a slight excess (1.1 equivalent) of the corresponding thiol in tetrahydrofuran. The salt NEt_3HBPh_4 was made by mixing NEt_3HCl and $NaBPh_4$ in water; UCl_4,[20] $U(NEt_2)_4$[21] and $U(BH_4)_4$[22] were prepared by published methods.

$[(thf)_3Na(\mu\text{-}SBu^t)_3U(\mu\text{-}SBu^t)_3Na(thf)_3]$ **1**.—(*a*) A round-bottom flask (100 cm^3) was charged with $U(BH_4)_4$ (150 mg, 0.51 mmol) and NaSBu^t (230 mg, 2.0 mmol) and thf (60 cm^3) was condensed into it under vacuum at −78 °C. After stirring for 2 h at 20 °C, the precipitate of $NaBH_4$ was filtered off; the red solution was concentrated to 40 cm^3 and deposited more $NaBH_4$ which was again filtered off. The red solution was then evaporated to dryness and the residue was extracted in thf (40 cm^3). Red microcrystals of complex 1 were obtained after evaporation (180 mg, 28%). The analytical sample was prepared by recrystallization from pyridine–tetrahydrofuran (Found: C, 45.7; H, 8.0; S, 15.15. $C_{48}H_{102}Na_2O_6S_6U$ requires C, 46.1; H, 8.15; S, 15.35%). ^{1}H NMR ([^{2}H$_5$]pyridine, 30 °C): δ 3.5 (24 H, thf), 2.6 (54 H, Bu^t) and 1.6 (24 H, thf). The bright crystals became opaque if thoroughly dried under vacuum and the NMR spectrum showed the loss of 4 molecules of thf from the complex.

(*b*) A round-bottom flask (100 cm^3) was charged with UCl_4 (300 mg, 0.79 mmol) and NaSBu^t (530 mg, 4.73 mmol) and diethyl ether (50 cm^3) was condensed into it under vacuum at −78 °C. After 12 h at room temperature the solvent was evaporated off and the reddish solid was extracted in thf (3 × 20 cm^3). After evaporation to dryness, the product was isolated as a red microcrystalline powder (514 mg, 52%).

Reactions of UCl_4 *or* $U(BH_4)_4$ *with Other* NaSR *Reagents.*—The reactions of UCl_4 or $U(BH_4)_4$ with NaSR (R = Bu^n, Pr^i or Ph) were conducted in the same manner as with NaSBu^t. The yields of the red products were similar (50–60%). ^{1}H NMR ([^{2}H$_8$]thf, 30 °C): R = Bu^n, δ 8.2 (2 H) and 0.7 (7 H); R = Pr^i, 7.8 (1 H) and 1.1 (6 H); R = Ph, 5.9; the spectra also exhibited signals at δ 3.5 and 1.6 corresponding to thf, the intensities of which were depending on the drying of the complexes. Red microcrystals of $[(thf)_3Na(\mu\text{-}SPh)_3U(\mu\text{-}SPh)_3Na(thf)_3]$ were prepared by recrystallization from thf and were suitable for an X-ray diffraction study; these crystals were dried under vacuum (10^{-2} mmHg, 10 h) and the elemental analyses were in agreement with the formula $[Na(thf)]_2[U(SPh)_6]$ (Found: C, 48.55; H, 4.4; S, 17.75. $C_{44}H_{38}Na_2O_2S_6U$ requires C, 48.55; H, 4.25; S, 18.2%).

Reaction of $U(SBu^n)_4$ *with* NaSBu^n *and Protonation of* $[Na(thf)_3]_2[U(SBu^n)_6]$.—The green compound $U(SBu^n)_4$ was prepared according to ref 5, by treatment of $U(NEt_2)_4$ with a large excess of Bu^{n}SH in diethyl ether; the product could also be synthesised in thf by using a slight excess (4.1 equivalent) of thiol.

(*a*) An NMR tube was charged with $U(SBu^n)_4$ (10.0 mg, 0.017 mmol) and NaSBu^n (3.8 mg, 0.034 mmol) in [^{2}H$_8$]thf (0.4 cm^3); the tube was immersed in an ultrasound bath (60 W, 40 KHz) and after 10 min at 20 °C the spectrum of the red solution was identical to that of $[Na(thf)_3]_2[U(SBu^n)_6]$.

Table 3 Fractional atomic coordinates, and their e.s.d.s for $[Na(thf)_3]_2[U(SBu^t)_6]$

Atom	*x*	*y*	*z*
U	0.000	0.000	0.000
S	−0.1049(4)	−0.0951(4)	0.0357(4)
Na	−0.1192(6)	−0.119	−0.119
O	−0.250(1)	−0.116(1)	−0.139(1)
C(1)	−0.190(2)	−0.072(2)	0.083(2)
C(2)	−0.226(2)	−0.007(3)	0.039(2)
C(3)	−0.173(2)	−0.042(2)	0.157(2)
C(4)	−0.240(2)	−0.135(2)	0.082(2)
C(5)	−0.283(2)	−0.047(2)	−0.158(2)
C(6)	−0.356(2)	−0.067(3)	−0.184(3)
C(7)	−0.371(3)	−0.149(3)	−0.150(3)
C(8)	−0.297(2)	−0.175(3)	−0.137(2)

Table 4 Fractional atomic coordinates and their e.s.d.s for $[Na(thf)_3]_2[U(SPh)_6]$

Atom	*x*	*y*	*z*
U	0.000	0.000	0.000
S	−0.1775(2)	−0.1023(2)	0.1015(2)
Na	0.1354(3)	0.135	0.135
O	0.0405(8)	0.1809(8)	0.3151(7)
C(1)	−0.1560(8)	−0.2214(8)	0.2288(8)
C(2)	−0.0571(9)	−0.3150(9)	0.2228(9)
C(3)	−0.046(1)	−0.410(1)	0.326(1)
C(4)	−0.131(1)	−0.410(1)	0.429(1)
C(5)	−0.231(1)	−0.314(1)	0.434(1)
C(6)	−0.246(1)	−0.218(1)	0.3339(9)
C(7)	−0.080(1)	0.246(2)	0.350(1)
C(8)	−0.102(2)	0.242(2)	0.469(2)
C(9)	0.016(2)	0.219(2)	0.483(1)
C(10)	0.098(2)	0.153(2)	0.399(1)

(*b*) An NMR tube was charged with $[Na(thf)_3]_2[U(SBu^n)_6]$ (10.0 mg, 0.008 mmol) and NEt_3HBPh_4 (6.8 mg, 0.016 mmol) in $[^2H_8]$thf (0.4 cm^3); a green powder immediately precipitated. The solution was discarded and the powder was dried under vacuum; its X-ray diffraction diagram was identical to that of $U(SBu^n)_4$.

Crystal Structure Determinations.—The complexes $[Na(thf)_3]_2[U(SR)_6]$ were obtained as red, beautifully shaped, transparent, octahedral crystals from pyridine–thf (R = Bu^t) or thf (R = Ph). Selected single crystals were introduced into thin-walled Lindeman glass tubes in a glove-box. Data were collected at room temperature on an Enraf-Nonius CAD4 diffractometer equipped with a graphite monochromator (λ = 0.71073 Å). The cell parameters were obtained by least-squares refinement of the setting angles of 25 reflections with θ between 8 and 12°. Three standard reflections were measured every hour: a decay was observed (22% in 32 h for **1**, and 12% in 29 h for the phenyl analogue) and was linearly corrected. The data were corrected for Lorentz polarization effects and absorption.[23] The structure was solved by the heavy-atom method and refined by full-matrix least squares on *F* with anisotropic thermal parameters for the uranium atom in **1** and for all atoms in the phenyl analogue. The hydrogen atoms were not introduced. All calculations were performed on a Vax 4000-200 computer with the Enraf-Nonius MOLEN system.[24] Analytical scattering factors for neutral atoms[25] were corrected for both $\Delta f'$ and $\Delta f''$ components of anomalous dispersion. Crystallographic data and experimental details are given in Table 2, final positional parameters in Tables 3 and 4.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

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