Monocyclooctatetraene Uranium Thiolate Complexes. Crystal Structure of $[\{U(\eta\text{-}C_8H_8)(\mu\text{-}SPr^i)_2\}_2]$†

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The monocyclooctatetraene uranium bis(thiolate) complexes $[U(cot)(SR)_2]$ (cot = η-C_8H_8, R = Bu^n or Pr^i) were prepared by treating $[U(cot)(BH_4)_2]$ **1** with the corresponding thiol or NaSR reagent. The isopropane thiolate derivative is a dimer in the crystalline form, with four bridging SPr^i ligands, and this structure is retained in solution. Reaction of **1** with $NaSBu^t$ afforded the anion $[U(cot)(SBu^t)_3]^-$ which adopts a three-legged piano-stool configuration.

Organoactinide thiolate complexes are very rare, being limited to the cyclopentadienyl compounds $[U(C_5H_4Me)_3(SPr^i)]$, $[U(C_5H_4Bu^t)_3(SPh)]$[1] and $[Th(C_5Me_5)_2(SPr^n)_2]$.[2] The latter was characterized by its crystal structure and the geometrical parameters led the authors to suggest that the actinide thiolate bonding involves less ligand-to-metal π donation than does actinide alkoxide bonding. The other 5f element compounds with SR ligands are the anionic derivatives $[Li(dme)]_4[U(SCH_2CH_2S)_4]$ (dme = 1,2-dimethoxyethane)[3] and $[Na(thf)_3]_2[U(SR)_6]$ (thf = tetrahydrofuran, R = Bu^t or Ph)[4] and the neutral complexes $[U(SR)_4]$ (R = Et or Bu^n),[5] $[U(SPr^i)_4\{OP(NMe_2)_3\}_2]$,[6] $[U_3S(SBu^t)_{10}]$[6] and $[U\{HB(pz)_3\}_2(SPr^i)_2]$ (pz = pyrazol-2-yl).[7]

As we recently synthesized a series of monocyclooctatetraene uranium bis(alkoxide) complexes $[U(cot)(OR)_2]$ (cot = η-C_8H_8), by alcoholysis of $[U(cot)(BH_4)_2]$,[8] it seemed to us interesting to prepare the thiolate analogues $[U(cot)(SR)_2]$, for comparison of their structure. Here we report the synthesis and characterization of such compounds with R = Bu^n, Pr^i or Bu^t and we describe the crystal structure of the isopropane thiolate derivative. We also present the preparation and the structure of the anionic complex $[Na(18\text{-crown-}6)(thf)_2][U(cot)(SBu^t)_3]$ (18-crown-6 = 1,4,7,10,13,16-hexaoxacyclooxadecane).

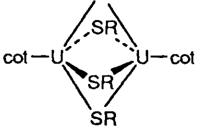
Results

Synthesis.—The bis(thiolate) compounds $[U(cot)(SR)_2]$ R = Bu^n **2a**, Pr^i **2b** or Bu^t **2c**) were obtained by treating $[U(cot)(BH_4)_2]$ **1** with an excess of the corresponding thiol RSH in toluene. The yields of **2a** and **2b**, determined by NMR spectroscopy, were almost quantitative but **2c** was formed in much lower yield (*ca.* 20%), with insoluble unidentified species. This synthesis of complexes **2** is similar to that of the alkoxide analogues $[U(cot)(OR)_2]$.[8]

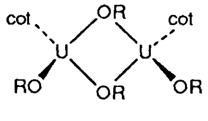
Because of the stench and toxicity of the thiol, we were encouraged to devise another route and to use the thiolate reagent NaSR. Reaction of **1** with 4 equivalents of $NaSBu^n$ or $NaSPr^i$ in toluene cleanly afforded the complexes **2a** and **2b** which have been isolated as green microcrystals in 72 and 59% yield respectively. In addition, this preparation is very convenient since the unreacted starting materials (**1** and NaSR), as well as the by-product $NaBH_4$, are insoluble in toluene and can be easily removed by filtration.‡

The reaction of **1** with $NaSBu^t$ followed a different course and gave, instead of the soluble bis(thiolate) **2c**, a powder of the anionic species $[U(cot)(SR)_3]^-$ as the major product. Red microcrystals of $[Na(thf)][U(cot)(SBu^t)_3]$ **3** were isolated in 68% yield after treatment of **1** with 4 equivalents of $NaSBu^t$ in toluene, extraction in tetrahydrofuran and crystallization from this solvent. It is noteworthy that **2a** and **2b** were unreactive towards an excess of NaSR reagent.

Structure of the Complexes in Solution.—The proton NMR spectra of complexes **2a**–**2c** in $[^2H_8]$toluene or $[^2H_8]$tetrahydrofuran (Table 1) showed that the two thiolate ligands are equivalent, giving rise to signals in the high-field region; the cot resonance appears at *ca.* δ -23. The spectra of **2a** and **2c** in pyridine revealed the presence of two entities, each one containing the $U(cot)(SR)_2$ fragment with equivalent thiolate ligands; spin-saturation transfer experiments[9] showed that these compounds were in rapid equilibrium. The spectrum of one component of each equilibrating mixture is similar to that of **2a** or **2c** in toluene or tetrahydrofuran. These facts indicated that these complexes adopt in toluene or thf the dimeric structure $[\{U(cot)(\mu\text{-}SR)_2\}_2]$ **A**, with four equivalent bridging SR ligands, and that this dimer would be partially cleaved in pyridine (py) to give the adduct $[U(cot)(SR)_2(py)_n]$. The thiolate bridges of **2b** are not split in pyridine. X-Ray



A



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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

‡ Similar treatment of **1** with NaOR (R = Et or Bu^t) in toluene gave the bis(alkoxide) complexes $[U(cot)(OR)_2]$ (NMR experiments) whereas the same reaction in thf led to the formation of $NaU(cot)(BH_4)_2(OR)$.[8]

Table 1 Proton NMR spectra of the complexes[a]

Compound	Solvent	cot Ligand[b]	Thiolate ligand
2a $[U(cot)(SBu^n)_2]$	$[^2H_8]$Toluene	−23.48	−11.95 (4 H, m), −7.97 (4 H, m) −4.44 (6 H, t, *J* 6), −1.12 (4 H, m)
	$[^2H_5]$Pyridine		
	Dimeric form[c]	−23.36	−12.04 (4 H, m), −8.12 (4 H, m) −4.63 (6 H, t, *J* 6), −1.01 (4 H, m)
	Monomeric form[c]	−26.62	−16.52 (4 H, m), −10.71 (8 H, m), −6.21 (6 H, t, *J* 6)
2b $[U(cot)(SPr^i)_2]$	$[^2H_8]$Toluene	−23.20	−11.69 (12 H), −9.95 (2 H)
	$[^2H_5]$Pyridine	−23.22	−11.84 (12 H), −10.09 (2 H)
2c $[U(cot)(SBu^t)_2]$	$[^2H_8]$Toluene	−22.96	−14.33 (18 H)
	$[^2H_5]$Pyridine		
	Dimeric form[d]	−22.88	−14.44 (18 H)[e]
	Monomeric form[d]	−28.99	+9.02 (18 H)
3 $[Na(thf)][U(cot)(SBu^t)_3]$	$[^2H_8]$thf	−30.05	−10.53 (27 H)

[a] At 30 °C. Data are given as chemical shifts δ (relative integral, multiplicity, coupling constant *J* in Hz). When not specified, the signals are singlets with half-height widths = 10–20 Hz. The spectra in $[^2H_8]$thf are similar to those recorded in $[^2H_8]$toluene. [b] The cot signal integrates for 8 H. [c] The ratio [dimer]/[monomer] is equal to 60:40 with [**2a**] = 0.04 mol dm^{-3}. [d] The ratio [dimer]/[monomer] is equal to 30:70 with [**2c**] = 0.04 mol dm^{-3}. [e] Irradiation of the signal caused a decrease in the intensity of the resonance at δ +9.02 (10% of its original value).

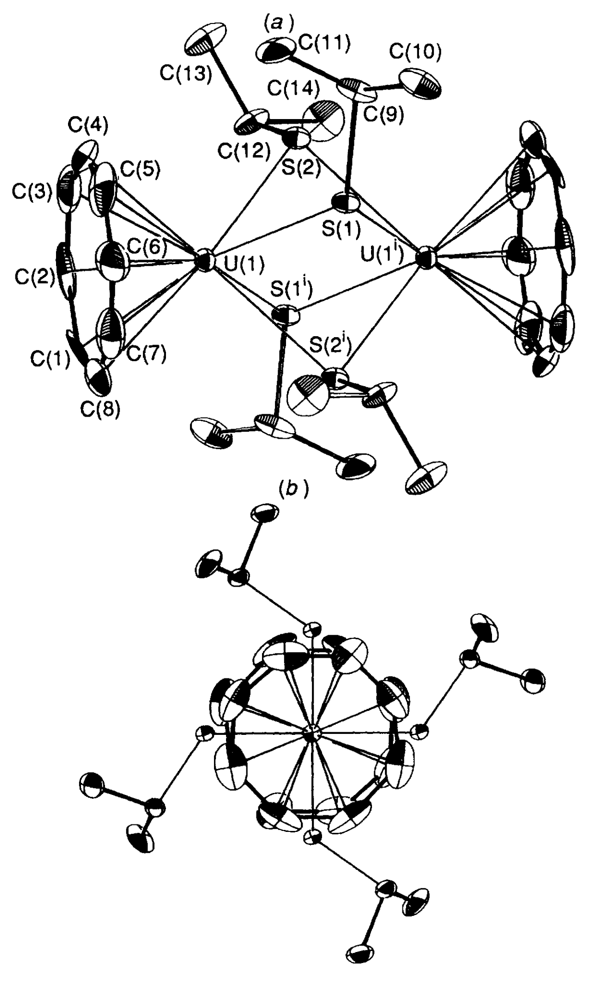

Fig. 1 (*a*) Perspective view of $[\{U(cot)(\mu\text{-}SPr^i)_2\}_2]$; atoms labelled i are related by a centre of symmetry. (*b*) View along the U(1)–U(1ⁱ) axis

crystallographic studies revealed that **2b** also exists as form **A** in the solid state.

Crystal Structure of $[\{U(cot)(\mu\text{-}SPr^i)_2\}_2]$.—ORTEP[10] drawings of **2b** (one of the two identical independent molecules) are shown in Fig. 1 and selected bond distances and angles are listed in Table 2. The dimeric structure is built up of two monomeric units which are bridged by four SPr^i groups. The middle of the U–U′ segment is an inversion centre and the U–U′ line is a pseudo-four-fold axis of symmetry. Each uranium atom is five-co-ordinate in a quite perfect square-pyramidal arrangement, if cyclooctatetraene is considered as a monodentate ligand. The two co-ordination polyhedra share the common square basis defined by the S atoms [in the molecule shown in Fig. 1, the distances S(1)–S(2) and S(2)–S(1ⁱ) are respectively equal to 3.112(4) and 3.087(4) Å and the angles S(1)–S(2)–S(1ⁱ) and S(2)–S(1)–S(2ⁱ) are equal to 89.5(1) and 90.5(1)°]; this basal plane is parallel to the planar cot ring. The U–SPr^i distances, which range from 2.806(3) to 2.895(3) Å [average 2.85(3) Å], are significantly longer than those determined in $[U\{HB(pz)_3\}_2(SPr^i)_2]$ [2.680(6) Å][7] and $[U(SPr^i)_4\{OP(NMe_2)_3\}_2]$ [2.723(5) and 2.721(4) Å];[6] such a difference between metal–sulfur bond lengths of bridging and terminal thiolate ligands was not unexpected.[11] The cot ligation is quite similar to that found in uranocene and other monocyclooctatetraene uranium(IV) compounds.[12]

Table 2 Selected bond distances (Å) and angles (°) for $[\{U(cot)(\mu\text{-}SPr^i)_2\}_2]$ with estimated standard deviations (e.s.d.s) in parentheses *

U(1)–S(1)	2.828(3)	U(2)–S(3)	2.895(3)
U(1ⁱ)–S(1)	2.856(3)	U(2ⁱ)–S(3)	2.806(3)
U(1)–S(2)	2.830(3)	U(2)–S(4)	2.850(4)
U(1ⁱ)–S(2)	2.881(3)	U(2ⁱ)–S(4)	2.855(3)
⟨U(1)–C$_{cot}$⟩	2.62(2)	⟨U(2)–C$_{cot}$⟩	2.63(3)
U(1)–Cot	1.91(3)	U(2)–Cot	1.93(2)
U(1)–S(1)–U(1ⁱ)	79.62(8)	U(2)–S(3)–U(2ⁱ)	79.44(9)
U(1)–S(2)–U(1ⁱ)	79.17(8)	U(2)–S(4)–U(2ⁱ)	79.40(9)
Cot–U(1)–S(1)	132.7(7)	Cot–U(2)–S(3)	127.5(7)
Cot–U(1)–S(2)	128.5(7)	Cot–U(2)–S(4)	126.4(7)

* Symmetry code: i −*x*, −*y*, −*z*, Cot is the centroid of the cyclooctatetraene ring.

We have attempted to determine the crystal structure of $[Na(18\text{-}crown\text{-}6)(thf)_2][U(cot)(SBu^t)_3]$, obtained by evaporation of a thf solution of **3** and 18-crown-6. The crystals were found to be triclinic, belonging to space group $P\bar{1}$, with a = 10.486(9), b = 10.704(4), c = 22.03(1) Å, α = 90.04(4), β = 93.66(6), γ = 93.18(5)°, Z = 2 and R_F = 0.058. Unfortunately, the structure could not be solved with good accuracy, because of interruption of the data collection after decomposition of the crystals in the X-ray beam (decay of 65% in 47 h), and will not be presented here in detail. The ORTEP drawing presented in Fig. 2 shows that the anion $[U(cot)(SBu^t)_3]^-$ adopts a three-legged piano-stool configuration, with the cot ligand occupying the

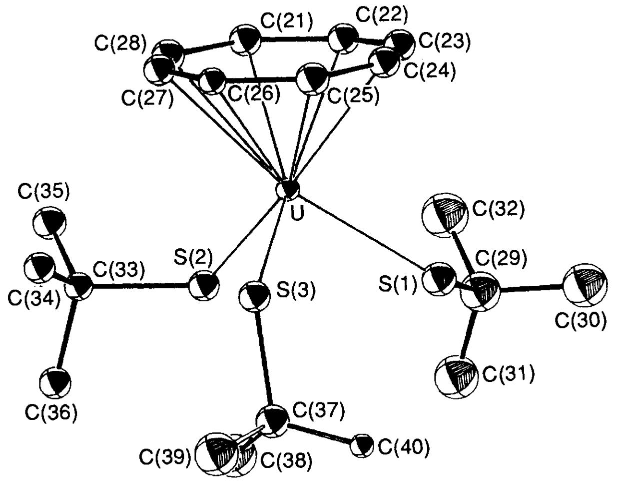

Fig. 2 Perspective view of the anion $[\mathrm{U(cot)(SBu^t)_3}]^-$

Table 3 Crystallographic data and experimental details

Crystal data	
Formula	$C_{28}H_{44}S_4U_2$
M	984.98
Crystal size/mm	0.65 × 0.40 × 0.20
Colour	Green
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	9.302(5)
b/Å	9.999(4)
c/Å	17.334(7)
α/°	86.69(3)
β/°	84.52(4)
γ/°	80.87(4)
U/Å³	1583(2)
Z (dimer)	2
D_c/g cm^{-3}	2.066
μ(Mo-Kα)/cm^{-1}	99.58
F(000)	920
Data collection	
θ limits/°	1, 22
Scan type	ω–2θ
Scan width/°	0.8 + 0.35 tan θ
Range of absolute transmission	0.934, 1.095
Range *h*, *k*, *l*	0–9, −10 to 10, −18 to 18
Reflections collected	
Total	4348
Unique	3876
With $I > 3\sigma(I)$	3005
No. of parameters	308
$R = \Sigma\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\Sigma\lvert F_o\rvert$	0.036
$R' = [\Sigma w\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert^2/\Sigma w(\lvert F_o\rvert)]^{\frac{1}{2}}$	0.048
p In weighting scheme, $w = 1/(\sigma F)^2 = 4F^2/[\sigma I^2 + (pF^2)^2]^{\frac{1}{2}}$	0.04
Maximum residual electron density/e Å^{-3}	2 [at 1 Å from U(1)]

apical position. The U–S distances [average 2.69(3) Å] should be similar to those measured in $[\mathrm{Na(thf)_3}]_2[\mathrm{U(SBu^t)_6}]$ [2.750(9) Å][6] but longer than the U–SBu^t (terminal) bond lengths in the cluster $[\mathrm{U_3S(SBu^t)_{10}}]$ [2.57(2) to 2.59(2) Å],[6] which are the shortest so far reported.

Discussion

The structure **A** of the complexes **2** is quite different from that of their alkoxide analogues which adopt in tetrahydrofuran or toluene the dimeric form **B**, with two bridging OR groups; this structure **B** is also that adopted by the isopropoxide derivative in the solid state. This difference is difficult to explain in terms of steric factors. The steric crowding of the terminal OPr^i ligand, which can be quantified by the maximum O–U–C$_\beta$ angle, in the crystallographically characterized compounds $[\{\mathrm{U(cot)(\mu\text{-}OPr^i)(OPr^i)}\}_2]$[8] (*ca.* 30°) and $[\{\mathrm{U(\eta\text{-}C_3H_5)_2(\mu\text{-}OPr^i)(OPr^i)}\}_2]$[13] (*ca.* 25°) is much smaller than that of the terminal SPr^i ligand in the compounds $[\mathrm{U\{HB(pz)_3\}_2(SPr^i)_2}]$[7] (*ca.* 50°) and $[\mathrm{U(SPr^i)_4\{OP(NMe_2)_3\}_2}]$[6] (*ca.* 55°). The less important steric requirement of the alkoxide ligand is due to the quasilinearity of the U–O–C$_\alpha$ angle, which reflects the strong π interaction between the metal and oxygen atoms. It is interesting that the OR and SR ligands occupy similar volumes (the thiolate group being eventually just slightly smaller than its alkoxide counterpart) if the angles U–O–C$_\alpha$ and U–S–C$_\alpha$ are both equal to 120°; this fact simply reflects the more remote position of the SR group from the metal centre. A similar observation was made by comparison of the OPh and SPh ligands.[14]

If the different structures **A** and **B** cannot be convincingly accounted for by the geometrical parameters, they are more easily understandable by considering the distinct electronic effects of the ligands. It seems likely that the U(cot)(SR)$_2$ unit would dimerize into a four SR bridged complex because it is less electron rich than the U(cot)(OR)$_2$ fragment which, even if less sterically crowded, forms a dimer with only two OR bridges. That a thiolate ligand is less electron donating than the corresponding alkoxide group was demonstrated by the reduction potentials of the complexes $[\mathrm{U(C_5H_5)_3(EPr^i)}]$ (E = O or S).[4] The greater propensity of a U–SR entity to increase the charge density around the metal was already pointed out by the different reactions of UCl$_4$ with alkali-metal alkoxide and thiolate reagents: the former led to the formation of the neutral tetraalkoxide compounds $[\mathrm{U(OR)_4}]$[15] whereas the latter readily afforded the anions $[\mathrm{U(SCH_2CH_2S)_4}]^{4-}$ [3] or $[\mathrm{U(SR)_6}]^{2-}$ (R = Bu^t or Ph).[4] Also different are the reactions of $[\mathrm{(C_5R_5)_2Lu(\mu\text{-}Me)_2Li(thf)_2}]$ (R = H or Me) with 2 equivalents of Bu^{t}OH or Bu^{t}SH which gave respectively $[\mathrm{Lu(C_5R_5)_2(OBu^t)(thf)}]$ and $[\mathrm{(C_5R_5)_2Lu(\mu\text{-}SBu^t)_2Li(thf)_2}]$.[16]

In the series of complexes $[\{\mathrm{U(cot)(SR)_2}\}_2]$, only **2a** and **2c** gave a Lewis-base adduct with pyridine and only **2c** was transformed into the anion $[\mathrm{U(cot)(SR)_3}]^-$ in the presence of the corresponding NaSR reagent. The reasons for the distinct behaviour of **2b** are not obvious; the more facile splitting of **2c** can be accounted for by the steric bulk of the SBu^t group.

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 (thf and toluene) or molecular sieves (pyridine).

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. $[\mathrm{U(cot)(BH_4)_2}]$ was prepared as described in ref. 17.

Reactions of $[\mathrm{U(cot)(BH_4)_2}]$ *with* RSH (R = Bu^n, Pr^i *or* Bu^t).—An NMR tube was charged with **1** (*ca.* 10 mg) in [^{2}H$_8$]toluene (0.3 cm^3) and the thiol (6 equivalents) was added *via* a microsyringe. The tube was heated at 50 °C for 3 h (Bu^{n}SH and Pr^{i}SH) or 10 h (Bu^{t}SH). The NMR spectra showed the quantitative formation of **2a** and **2b**. The reaction with Bu^{t}SH

Table 4 Fractional atomic coordinates with e.s.d.s in parentheses for [{U(cot)(μ-SPr^i)$_2$}$_2$]

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
U(1)	0.91 530(4)	0.400 32(4)	0.077 50(2)	C(12)	1.143(1)	0.653(1)	0.152 5(6)
U(2)	0.396 61(4)	0.065 85(4)	0.418 22(2)	C(13)	1.232(2)	0.596(1)	0.219 5(7)
S(1)	1.132 8(3)	0.314 4(3)	−0.04 24(2)	C(14)	1.187(2)	0.786(1)	0.121 3(8)
S(2)	1.167 8(3)	0.525 5(3)	0.076 9(2)	C(21)	0.216(2)	−0.034(1)	0.337 1(8)
S(3)	0.302 9(3)	0.028 6(3)	0.581 1(2)	C(22)	0.334(2)	−0.032(2)	0.288 1(8)
S(4)	0.461 9(3)	−0.205 5(3)	0.479 4(2)	C(23)	0.424(2)	0.067(2)	0.265 0(8)
C(1)	0.672(2)	0.449(2)	0.166 9(9)	C(24)	0.424(2)	0.199(2)	0.285 5(7)
C(2)	0.780(2)	0.457(2)	0.215 0(8)	C(25)	0.333(2)	0.290(2)	0.336 5(9)
C(3)	0.911(2)	0.380(2)	0.228 2(8)	C(26)	0.218(2)	0.284(2)	0.381 2(8)
C(4)	0.982(2)	0.267(2)	0.205 6(8)	C(27)	0.127(2)	0.187(2)	0.400 3(7)
C(5)	0.971(2)	0.167(2)	0.156 3(9)	C(28)	0.127(1)	0.054(2)	0.381 8(7)
C(6)	0.865(2)	0.150(1)	0.112 4(9)	C(29)	0.242(2)	0.172(1)	0.645 0(7)
C(7)	0.736(2)	0.221(2)	0.092 3(8)	C(30)	0.179(1)	0.118(2)	0.719 4(7)
C(8)	0.649(2)	0.347(2)	0.115 4(9)	C(31)	0.138(2)	0.284(1)	0.611 9(8)
C(9)	1.320(1)	0.245(1)	−0.019 7(7)	C(32)	0.300(1)	−0.278(1)	0.514 3(7)
C(10)	1.391(1)	0.165(1)	−0.091 4(9)	C(33)	0.278(1)	−0.378(1)	0.456 4(7)
C(11)	1.323(1)	0.161(1)	0.053 6(8)	C(34)	0.301(2)	−0.346(2)	0.595 2(8)

gave a precipitate but **2c** was the sole uranium complex in solution, formed in *ca.* 20% yield.

[U(cot)(SBu^n)$_2$] **2a**.—A round-bottom flask (100 cm^3) was charged with **1** (300 mg, 0.8 mmol) and NaSBu^n (360 mg, 3.2 mmol) and toluene (40 cm^3) was condensed into it under vacuum at −78 °C. The reaction mixture was stirred for 20 h at 20 °C and after filtration, the green solution was evaporated to dryness. The residue was extracted in toluene (40 cm^3) and a dark green microcrystalline powder of **2a** was obtained after evaporation (303 mg, 72%) (Found: C, 36.55; H, 4.8; S, 12.1. $C_{16}H_{26}S_2U$ requires C, 36.9; H, 5.0; S, 12.3%).

[U(cot)(SPr^i)$_2$] **2b**.—The preparation of complex **2b** was identical to that of **2a**. Reaction of **1** (300 mg, 0.8 mmol) with NaSPr^i (310 mg, 3.2 mmol) gave **2b** which was isolated as green microcrystals (236 mg, 59%) (Found: C, 33.8; H, 4.35; S, 12.7. $C_{14}H_{22}S_2U$ requires C, 34.15; H, 4.5; S, 13.0%).

[Na(thf)][U(cot)(SBu^t)$_3$] **3**.—A round-bottom flask (100 cm^3) was charged with **1** (300 mg, 0.8 mmol) and NaSBu^t (360 mg, 3.2 mmol) and toluene (50 cm^3) was condensed into it under vacuum at −78 °C. After stirring for 48 h at 20 °C, a grey precipitate in a green solution was obtained. The solution was filtered and evaporated to dryness, leaving a green powder of **2c** (42 mg, 10%). The precipitate was extracted in thf (40 cm^3) and the red solution was dried under vacuum for 3 h; the residue was then extracted in diethyl ether (50 cm^3) and after evaporation, red microcrystals of **3** were collected and dried under vacuum (384 mg, 68%) (Found: C, 40.5; H, 5.9; S, 13.5. $C_{24}H_{43}NaOS_3U$ requires C, 40.9; H, 6.15; S, 13.65%).

Crystal Structure of Complex **2b**.—Dark green crystals of **2b** were obtained by recrystallization from thf–pentane. A single crystal was introduced into a thin-walled Lindeman glass tube. Reflection data were collected at 20°C on an Enraf–Nonius CAD-4 diffractometer equipped with a graphite monochromator [λ(Mo-Kα) = 0.71073 Å]. The cell parameters were obtained by a least-squares refinement of the setting angles of 25 reflections with θ between 8 and 12°. Three standard reflections were measured after each hour; the decay of 15.6% in 58 h was linearly corrected. The data were corrected for Lorentz polarization effects and absorption.[18] The structure was solved by the heavy-atom method and refined by full-matrix least squares on *F* with anisotropic thermal parameters. Hydrogen atoms were introduced at calculated positions and constrained to ride their C atoms. There are two independent molecules in the asymmetric unit. All calculations were performed on a Vax 4000–200 computer with the Enraf–Nonius MolEN system.[19] Analytical scattering factors for neutral atoms[20] were corrected for both $\Delta f'$ and $\Delta f''$ components of anomalous dispersion. Crystallographic data and experimental details are given in Table 3, final positional parameters in Table 4.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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