Synthesis of Neutral and Anionic Uranyl Aryloxide Complexes from Uranyl Amide Precursors: X-ray Crystal Structures of UO2(O-2,6-*i*-Pr2C6H3)2(py)3 and [Na(THF)3]2[UO2(O-2,6-Me2C6H3)4]

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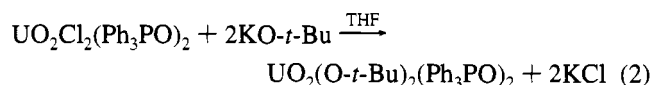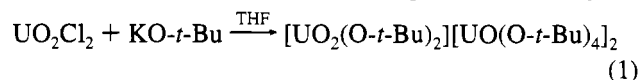
Received March 10, 1995®

Reaction of anhydrous UO_2Cl_2 with 2 equiv of $KN(SiMe_3)_2$ in THF leads to formation of the neutral bis(amido) complex $UO_2[N(SiMe_3)_2]_2(THF)_2$ (**1**), whereas the use of 2, 3, or 4 equiv of $NaN(SiMe_3)_2$ in an analogous reaction produces the tetrakis(amido) salt $[Na(THF)_2]_2\{UO_2[N(SiMe_3)_2]_4\}$ (**2**). Alcoholysis of **1** with 2 equiv of HO-2,6-*i*-Pr2C6H3 in the presence of pyridine gives the bis(aryloxide) complex $UO_2(O$-$2,6$-i-$Pr_2C_6H_3)_2(py)_3$ (**3**) (py = C_5H_5N), whereas alcoholysis of **2** with 4 equiv of HO-2,6-Me2C6H3 in THF produces the tetrakis(aryloxide) salt $[Na(THF)_3]_2[UO_2(O$-$2,6$-$Me_2C_6H_3)_4]$ (**4**). The molecular structures of **3** and **4** have been determined by means of single-crystal X-ray diffraction studies. Compound **3** exhibits pentagonal bipyramidal geometry, with the uranyl oxygen atoms occupying the axial positions and the aryloxide and pyridine ligands lying in the equatorial plane. U—O bond lengths average 1.789(5) Å for the uranyl oxygen atoms and 2.197(9) Å for the aryloxide ligands, while U—N distances to the pyridine ligands average 2.616(7) Å. Compound **4** is comprised of a uranium metal center coordinated in a pseudo-octahedral fashion by six oxygen atoms, with two sodium cations each coordinated to one uranyl oxygen atom and one oxygen atom of an aryloxide ligand. U—O bond distances to the uranyl oxygens average 1.814(5) Å, while distances to the aryloxide ligands average 2.204(8) Å for the two aryloxide ligands not involved in coordination to the sodium cations and 2.288(5) Å for the aryloxide ligands forming U—O—Na interactions. Crystal data for **3** (at −70 °C): Monoclinic, space group $P2_1$, $a = 11.582(2)$ Å, $b = 13.975(3)$ Å, $c = 12.322(2)$ Å, $\beta = 103.67(3)°$, $V = 1937.9(6)$ Å³, $Z = 2$, $D_{calc} = 1.477$ g cm⁻³. Crystal data for **4** (at −70 °C): Triclinic, space group $P\bar{1}$, $a = 12.830(2)$ Å, $b = 13.574(2)$ Å, $c = 18.382(3)$ Å, $\alpha = 93.40(1)°$, $\beta = 98.12(1)°$, $\gamma = 106.21(1)°$, $V = 3027(2)$ Å³, $Z = 2$, $D_{calc} = 1.35$ g cm⁻³.

Introduction

The use of sterically encumbered alkoxide,[2] aryloxide,[3] and amide[4] ligands in investigations of the structural and reaction chemistry of thorium and uranium in the +III and +IV oxidation states has become relatively common in recent years. These ligands stabilize novel low-coordinate actinide environments by preventing coordinative polymerization. In contrast, there are few reported examples of amide or alkoxide complexes of the uranyl (UO_2^{2+}) ion;[5] these systems are generally observed to form anionic "ate" complexes[5h] or to undergo ligand redistribution reactions which lead to the formation of polymetallic species.[5c,i] We have investigated a variety of synthetic strategies in attempts to prepare monomeric uranyl complexes of these ligands. Halide metathesis routes (eqs 1 and 2) may be

$$UO_2Cl_2 + KO\text{-}t\text{-}Bu \xrightarrow{THF} [UO_2(O\text{-}t\text{-}Bu)_2][UO(O\text{-}t\text{-}Bu)_4]_2 \quad (1)$$

$$UO_2Cl_2(Ph_3PO)_2 + 2KO\text{-}t\text{-}Bu \xrightarrow{THF}$$
$$UO_2(O\text{-}t\text{-}Bu)_2(Ph_3PO)_2 + 2KCl \quad (2)$$

employed to prepare uranyl alkoxide complexes derived from the moderately bulky *tert*-butoxide ligand. Ligand redistribution (eq 1)[5i] is found to occur readily at room temperature, but this process may be prevented by addition of a Lewis base such as triphenylphosphine oxide to provide steric saturation of the uranyl alkoxide product (eq 2).[5j]

® Abstract published in *Advance ACS Abstracts*, July 1, 1995.
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While neutral uranyl alkoxide complexes have been prepared by utilizing aliphatic alkoxide ligands, the only reported aromatic alkoxide complexes reported to date are anionic "ate" species.[5h] One synthetic approach which is often employed to circumvent the formation of complex ions is alcoholysis of neutral metal amide complexes with an alcohol or substituted phenol. This reaction can provide a salt-free synthetic route to actinide alkoxide or aryloxide complexes and avoid many of the problems associated with classical halide metathesis procedures.[6] Among the rare examples of well-characterized uranyl amide complexes described to date, the bis(trimethylsilyl)amide derivative $UO_2[N(SiMe_3)_2]_2(THF)_2$ (**1**) prepared by Andersen and co-workers in 1979[5d] (eq 3) appeared to be a suitable substrate for the preparation of uranyl aryloxide species *via* alcoholysis reactions.

$$UO_2Cl_2 + 2NaN(SiMe_3)_2 \xrightarrow{THF}$$
$$UO_2[N(SiMe_3)_2]_2(THF)_2 + 2NaCl \quad (3)$$
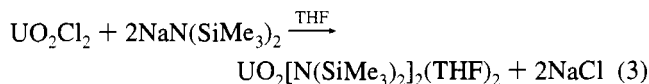
During our investigations, we found that the metathesis reaction of UO_2Cl_2 with alkali metal bis(trimethylsilyl)amide salts yielded different products depending upon whether the sodium or potassium amide salt was used. We describe here the formation of two uranyl amide complexes and their subsequent alcoholysis by substituted phenols to produce both neutral and anionic uranyl aryloxide species.

Results and Discussion

Synthesis and Reactivity. The addition of 2 equiv of potassium bis(trimethylsilyl)amide to a THF slurry of UO_2Cl_2 at room temperature resulted in a gradual color change from yellow to orange over several hours. Low-temperature crystallization from hexane/THF allows the isolation of orange crystals of the previously-reported[5d] complex $UO_2[N(SiMe_3)_2]_2(THF)_2$ (**1**) in good yield (eq 4).

$$UO_2Cl_2 + 2KN(SiMe_3)_2 \xrightarrow{THF}$$
$$UO_2[N(SiMe_3)_2]_2(THF)_2 + 2KCl \quad (4)$$
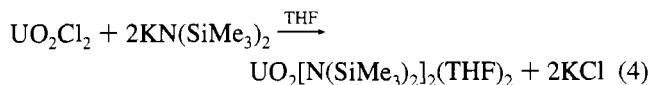
^1H NMR spectra (benzene-d_6) revealed a single bis(trimethylsilyl)amide resonance at δ 0.56, together with somewhat broadened resonances assigned to coordinated THF at δ 1.50 and 4.37. In the infrared spectrum, characteristic U=O stretching modes were observed at 862 and 839 cm^{-1}. These data did not allow an unambiguous assignment of molecular structure to the *trans-* or *cis-*geometries shown schematically in **A** and **B**, and thus a single-crystal X-ray diffraction analysis was undertaken.

A   **B**
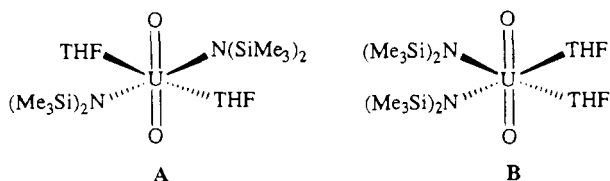
The X-ray data collected for **1** were of poor quality and allowed only the atom connectivity within the molecule to be determined. Bond lengths and angles had relatively large standard deviations and therefore will not be discussed in the
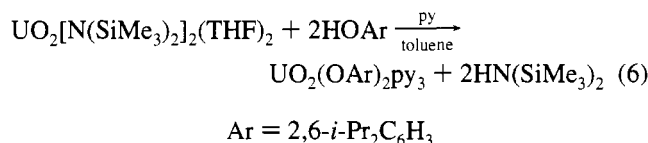
Structural Studies section below. The data did unambiguously confirm, however, the all-*trans* arrangement of ligands (*i.e.* structure **A**) originally proposed by Andersen.

During attempts to prepare $UO_2[N(SiMe_3)_2]_2(THF)_2$ (**1**) *via* the literature procedure (*i.e.* using the reagents and stoichiometry of eq 3)[5d] an orange crystalline material **2** was obtained whose spectroscopic data differed considerably from those of **1**. Most notably, ^1H NMR resonances (benzene-d_6) were observed for **2** at δ 0.68, 1.23, and 3.20 (although they integrated for the same 9:2:2 ratio found for **1**). Infrared spectra showed U=O vibrations at 866, 858, and 841 cm^{-1}. Microanalytical data for **2** suggested the formulation $[Na(THF)_2]_2\{UO_2[N(SiMe_3)_2]_4\}$, and indeed it was found that the yield of **2** was optimized when 4 equiv of $NaN(SiMe_3)_2$ was used in the reaction with uranyl chloride, as shown in eq 5. Attempts to grow X-ray-quality

$$UO_2Cl_2 + 4NaN(SiMe_3)_2 \xrightarrow{THF}$$
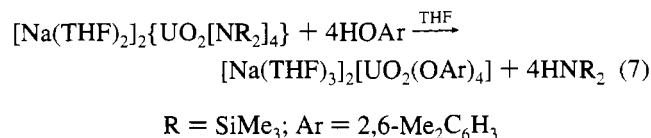$$[Na(THF)_2]_2\{UO_2[N(SiMe_3)_2]_4\} + 2NaCl \quad (5)$$
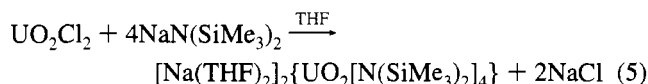
crystals of **2** were thwarted by rapid solvent loss and subsequent powdering of the crystals. It is noteworthy that during a previous synthesis of the triphenylphosphine adduct UO_2-$[N(SiMe_3)_2]_2(Ph_3PO)_2$ from the base adduct $UO_2Cl_2(Ph_3PO)_2$ and 2 equiv of $NaN(SiMe_3)_2$,[5j] we did *not* observe the formation of an amido "ate" complex similar to **2**.

Addition of 2 equiv of 2,6-diisopropylphenol to a toluene solution of **1** at room temperature produced an immediate color change to blood red. Addition of an excess of pyridine to the solution, followed by crystallization from hexane, yielded dark red crystals of the neutral bis(aryloxide) species $UO_2(O-2,6-i-Pr_2C_6H_3)_2(py)_3$ (**3**) (eq 6). Microanalytical data for the product were consistent with the proposed formulation. Room-temper-

$$UO_2[N(SiMe_3)_2]_2(THF)_2 + 2HOAr \xrightarrow[toluene]{py}$$
$$UO_2(OAr)_2py_3 + 2HN(SiMe_3)_2 \quad (6)$$

$$Ar = 2,6-i-Pr_2C_6H_3$$

ature ^1H NMR spectra of **3** in benzene-d_6 revealed only one type of pyridine ligand, presumably due to a rapid fluxional process which makes the three pyridine ligand sites equivalent on the NMR time scale. In the infrared spectrum (KBr plates, Nujol mull), U=O stretching modes are observed at 875 and 857 cm^{-1}.

Reaction of a THF solution of $[Na(THF)_2]_2\{UO_2[N(SiMe_3)_2]_4\}$ (**2**) with 4 equiv of 2,6-dimethylphenol produced a color change from orange to deep red/brown. Dark red/brown crystals were isolated from THF solution and were shown by means of an X-ray diffraction study (*vide infra*) to be the salt complex [Na-(THF)_3]_2[UO_2(O-2,6-Me_2C_6H_3)_4] (**4**) (eq 7). Crystals of **4** were

$$[Na(THF)_2]_2\{UO_2[NR_2]_4\} + 4HOAr \xrightarrow{THF}$$
$$[Na(THF)_3]_2[UO_2(OAr)_4] + 4HNR_2 \quad (7)$$

$$R = SiMe_3; Ar = 2,6-Me_2C_6H_3$$

seen to powder rapidly at room temperature, suggesting facile solvent loss, and microanalytical data could only be obtained which corresponded to the presence of one THF ligand per sodium cation *i.e.* $[Na(THF)]_2[UO_2(O-2,6-Me_2C_6H_3)_4]$. The presence of only one phenoxide environment in the room-temperature ^1H NMR spectrum is indicative of either a fluxional process in which O—Na—O bridging contacts are scrambled over all phenoxide sites or of cation—anion dissociation in

(6) See refs 2b, 3c−e, and also: (a) Van der Sluys, W. G.; Sattelberger, A. P.; Streib, W. E.; Huffman, J. C. *Polyhedron* **1989**, *8*, 1247. (b) Dormond, A.; El Bouadili, A. A.; Moïse, C. J. *J. Chem. Soc., Chem. Commun.* **1985**, 914. (c) Dormond, A.; El Bouadili, A. A.; Moïse, C. J. *J. Less-Common Met.* **1986**, *122*, 159.

Table 1. Summary of Crystallographic Data

compd	3	4
empirical formula	$C_{39}H_{49}N_3O_4U$	$C_{56}H_{84}Na_2O_6U$
color; habit	dark red plate	red-brown block
cryst dimens, mm	$0.15 \times 0.30 \times 0.25$	$0.22 \times 0.38 \times 0.49$
space group	$P2_1$	$P\bar{1}$
cell dimens		
a, Å	11.582(2)	12.830(2)
b, Å	13.975(3)	13.574(2)
c, Å	12.322(2)	18.382(3)
α, deg		93.40(1)
β, deg	103.67(3)	98.12(1)
γ, deg		106.21(1)
temp, °C	−70	−70
Z (molecules/cell)	2	2
V, Å^3	1937.9(6)	3027(2)
D_{calc}, g cm^{-3}	1.477	1.35
λ(Mo Kα), Å	0.710 73	0.709 26
fw	861.8	1233.28
abs coeff, cm^{-1}	40.09	26.07
2θ range, deg	2–50	0–45
measd reflcns	3747	8330
unique reflcns	3463	7902
obsd reflcns	3183 [$F > 4.0\sigma(F)$]	5542 [$F > 1.73\sigma(F)$]
$R(F)^a$	0.0218	0.035
$R_w(F)^b$	0.0285	0.043
goodness-of-fit	0.93	1.80

$^a R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $^b R_w(F) = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.
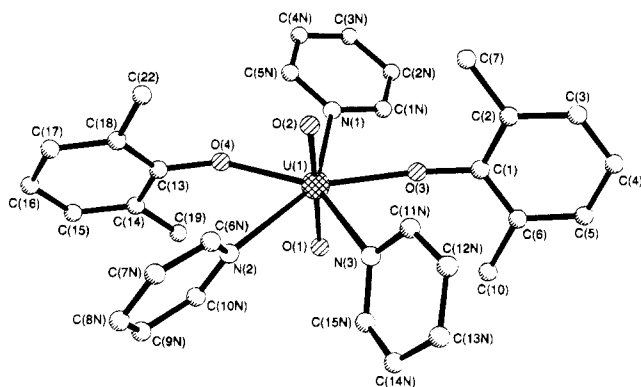

Figure 1. Ball-and-stick representation of the molecular structure of $UO_2(O-2,6-i-Pr_2C_6H_3)_2(py)_3$ (**3**) giving the atom-numbering scheme used in the tables. Methyl carbon atoms have been omitted for clarity.

solution. U=O stretching frequencies in the IR spectrum are seen at 878, 854, and 839 cm^{-1}.

Structural Studies

A summary of data collection parameters for $UO_2(O-2,6-i-Pr_2C_6H_3)_2(py)_3$ (**3**) and $[Na(THF)_3]_2[UO_2(O-2,6-Me_2C_6H_3)_4]$ (**4**) is presented in Table 1.

$UO_2(O-2,6-i-Pr_2C_6H_3)_2(py)_3$ (**3**). X-ray-quality crystals of **3** were obtained from a concentrated toluene/hexane (1:1) solution at −40 °C. A ball-and-stick view of the molecular structure of **3**, giving the atom-numbering scheme used in the tables, is depicted in Figure 1. Selected fractional coordinates and isotropic thermal parameters are given in Table 2, while selected bond lengths and angles are presented in Table 3. The molecular geometry of **3** is best described as pseudopentagonal bipyramidal, with uranyl oxygens in axial positions and the aryloxide and pyridine ligands lying in the equatorial plane. This geometry is well established for uranyl complexes, having been documented in a wide variety of complexes such as $UO_2(R_2-NCS_2)_2L$ (R = Me, Et; L = Ph_3PO, Ph_3AsO, $Me_3NO)^7$ and species in which the uranyl core is complexed by a chelating pentadentate Schiff base.[8] Metal−ligand distances within the

Table 2. Selected Fractional Coordinates and Equivalent Isotropic Displacement Coefficients (Å$^2 \times 10^4$) for $UO_2(O-2,6-i-Pr_2C_6H_3)_2$-$(py)_3$ (**3**)

	10^5x	10^5y	10^5z	U(eq)
U(1)	2816(2)	45040(2)	27028(2)	229(1)
O(1)	2154(41)	56431(35)	20354(37)	301(15)
O(2)	4426(43)	33144(33)	32601(37)	290(15)
O(3)	16551(43)	50248(38)	41058(41)	360(16)
C(1)	27173(59)	51511(52)	48336(55)	293(21)
C(2)	30690(55)	45215(138)	57411(48)	366(19)
C(3)	41819(70)	46656(128)	64707(62)	541(37)
C(4)	48794(74)	54213(79)	63422(71)	559(33)
C(5)	45307(72)	60355(70)	54467(66)	461(29)
C(6)	34392(64)	59211(59)	46812(58)	351(23)
C(7)	22679(75)	36965(59)	59108(64)	429(27)
C(10)	30464(90)	66084(71)	37249(66)	583(34)
O(4)	−16223(42)	42234(31)	19553(39)	278(15)
C(13)	−25167(61)	39387(51)	10935(56)	254(22)
C(14)	−31453(54)	46259(111)	3743(54)	319(23)
C(15)	−40678(69)	43164(58)	−5098(65)	407(35)
C(16)	−43409(82)	33535(70)	−6732(69)	534(32)
C(17)	−36985(85)	26881(67)	354(70)	474(31)
C(18)	−27684(70)	29667(68)	9248(69)	317(26)
C(19)	−28637(79)	56736(67)	5592(70)	366(28)
C(22)	−20975(69)	22213(52)	17319(64)	367(25)
N(1)	−8340(57)	51346(43)	41899(51)	362(20)
C(1N)	−3424(84)	58006(66)	49563(81)	571(34)
C(2N)	−8858(97)	61104(74)	57718(86)	674(39)
C(3N)	−19816(105)	57590(74)	58071(80)	647(40)
C(4N)	−24922(99)	50912(66)	50412(81)	601(38)
C(5N)	−19097(72)	48004(52)	42367(66)	425(28)
N(2)	580(52)	37842(42)	7088(49)	311(19)
C(6N)	3694(72)	28678(57)	5845(70)	405(26)
C(7N)	1448(86)	24206(63)	−4287(68)	492(32)
C(8N)	−4050(90)	29191(71)	−13720(77)	556(35)
C(9N)	−7304(95)	38735(76)	−12759(75)	570(36)
C(10N)	−4607(74)	42630(49)	−2057(63)	371(27)
N(3)	23225(52)	41872(46)	22256(53)	373(21)
C(11N)	31133(65)	36144(60)	28931(67)	408(27)
C(12N)	42206(76)	34185(73)	27069(80)	533(32)
C(13N)	45129(80)	37946(91)	17944(101)	708(43)
C(14N)	36925(83)	43314(90)	10827(102)	771(56)
C(15N)	26234(65)	46070(123)	13433(76)	644(34)

Table 3. Selected Bond Distances (Å) and Angles (deg) for UO_2-$(O-2,6-i-Pr_2C_6H_3)_2(py)_3$ (**3**)

U(1)−O(1)	1.785(5)	U(1)−N(1)	2.631(7)
U(1)−O(2)	1.792(5)	U(1)−N(2)	2.611(6)
U(1)−O(3)	2.179(5)	U(1)−N(3)	2.605(7)
U(1)−O(4)	2.215(5)		
O(1)−U(1)−O(2)	173.4(2)	O(1)−U(1)−O(3)	90.7(2)
O(1)−U(1)−O(4)	92.1(2)	O(2)−U(1)−O(3)	90.9(2)
O(2)−U(1)−O(4)	89.9(2)	O(3)−U(1)−O(4)	149.0(2)
O(1)−U(1)−N(1)	92.7(2)	O(2)−U(1)−N(1)	93.9(2)
O(3)−U(1)−N(1)	73.9(2)	O(4)−U(1)−N(1)	75.2(2)
O(1)−U(1)−N(2)	85.8(2)	O(2)−U(1)−N(2)	88.9(2)
O(3)−U(1)−N(2)	140.1(2)	O(1)−U(1)−N(3)	89.4(2)
O(2)−U(1)−N(3)	84.9(2)	O(3)−U(1)−N(3)	72.8(2)
O(4)−U(1)−N(1)	75.2(2)	O(4)−U(1)−N(2)	70.9(2)
O(4)−U(1)−N(3)	138.0(2)	N(1)−U(1)−N(2)	146.0(2)
N(1)−U(1)−N(3)	146.6(2)	N(2)−U(1)−N(3)	67.4(2)
U(1)−O(3)−C(1)	161.6(5)	U(1)−O(4)−C(13)	151.5(5)

molecule are all within the expected ranges. U−O bond lengths for the uranyl oxygen atoms of 1.785(5) and 1.792(5) Å are almost identical to those observed in $UO_2(O-t-Bu)_2(Ph_3PO)_2$,[5j] while U−O distances to the aryloxide ligands (2.179(5) and 2.215(5) Å) are similar to those of 2.153(6) Å (av) in $UO_2(O-t-Bu)_2(Ph_3PO)_2$[5j] and 2.08(2) Å (av) in $[UO_2(\mu_2-OPh)_2(THF)_2]_2$-$[U(\mu_3-O)(OPh)_3(THF)]_2$.[9] U−N distances to the pyridine ligands in **3** are 2.631(7), 2.611(6) and 2.605(7) Å and are directly comparable to those observed in $UO_2(NO_3)_2py_2$,[10] $UO_2(Ph_2C_3HO_2)_2py$,[11] and $UO_2(t-BuOC_4H_4O_2)_2py$,[11] which are 2.543(15), 2.569(6), and 2.595(24) Å, respectively. The five
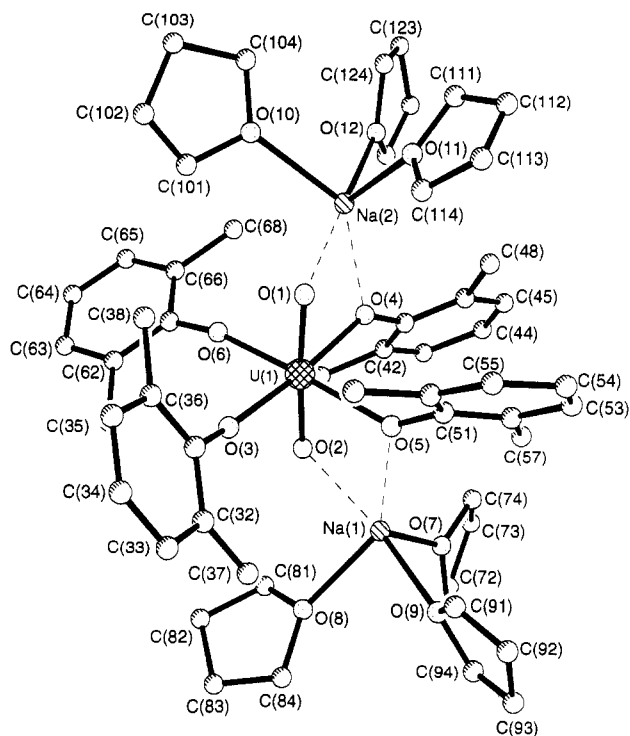
Figure 2. Ball-and-stick representation of the molecular structure of [Na(THF)₃]₂[UO₂(O-2,6-Me₂C₆H₃)₄] (**4**) giving the atom-numbering scheme used in the tables.

ligands within the equatorial plane are relatively coplanar, with the largest deviation from 90° of any of the O_{uranyl}–U–L angles (L = N or O atom in equatorial plane) being 5.1° in the case of O(2)–U(1)–N(3) [84.9(2)°]. The relatively obtuse U–O–C angles within the aryloxide ligands (161.6(5) and 151.5(5)°) are typical of those seen in many actinide aryloxide complexes.[3]

[Na(THF)₃]₂[UO₂(O-2,6-Me₂C₆H₃)₄] (4). X-ray-quality crystals of **4** were obtained from a concentrated THF solution at −40 °C. A ball-and-stick representation of the molecular structure of **4**, giving the atom-numbering scheme used in the tables, is shown in Figure 2. Selected fractional coordinates and isotropic thermal parameters are given in Table 4, while selected bond lengths and angles are presented in Table 5. The uranium metal center in **4** is coordinated in a pseudo-octahedral fashion by two uranyl oxygen atoms and four aryloxide ligands. The two sodium cations are each coordinated to one uranyl oxygen atom and one oxygen atom of an aryloxide ligand, with the remainder of their coordination sphere being taken up by three THF molecules, making each sodium cation five-coordinate. The geometry about the sodium cations may best

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Table 4. Selected Fractional Coordinates and Equivalent Isotropic Displacement Coefficients ($Å^2$) for [Na(THF)₃]₂[UO₂(O-2,6-Me₂-C₆H₃)₄] (**4**)

	x	y	z	B(eq)
U(1)	−0.19377(3)	0.22632(2)	−0.23591(2)	3.95(1)
Na(1)	0.0686(3)	0.3851(3)	−0.2465(2)	6.3(1)
Na(2)	−0.3245(3)	−0.0370(2)	−0.2591(2)	6.2(1)
O(1)	−0.3083(4)	0.1325(4)	−0.2949(3)	5.0(2)
O(2)	−0.0727(4)	0.3140(4)	−0.1790(3)	5.0(2)
O(3)	−0.2573(5)	0.3565(4)	−0.2675(3)	5.5(2)
O(4)	−0.1437(4)	0.0834(4)	−0.2057(3)	4.8(2)
O(5)	−0.0849(4)	0.2521(4)	−0.3260(3)	5.2(2)
O(6)	−0.2871(5)	0.2066(4)	−0.1442(3)	5.7(3)
O(7)	0.2304(6)	0.3492(7)	−0.1850(5)	9.9(4)
O(8)	0.1053(6)	0.5368(5)	−0.1642(4)	8.1(3)
O(9)	0.1462(7)	0.4688(6)	−0.3410(5)	10.1(4)
O(10)	−0.5125(6)	−0.0611(6)	−0.2497(5)	9.7(4)
O(11)	−0.3663(7)	−0.1042(6)	−0.3857(4)	10.1(4)
O(12)	−0.3183(7)	−0.1906(5)	−0.2022(4)	8.8(4)
C(31)	−0.3084(8)	0.4117(7)	−0.3079(5)	5.0(4)
C(32)	−0.244(1)	0.5029(7)	−0.3303(5)	6.5(4)
C(33)	−0.297(1)	0.5618(9)	−0.3772(7)	9.3(6)
C(34)	−0.415(1)	0.525(1)	−0.3978(7)	9.8(7)
C(35)	−0.476(1)	0.4356(9)	−0.3711(7)	8.4(5)
C(36)	−0.422(1)	0.3785(8)	−0.3262(5)	6.7(5)
C(37)	−0.122(1)	0.5383(8)	−0.3076(7)	8.8(6)
C(38)	−0.488(1)	0.2794(9)	−0.2991(7)	8.6(6)
C(41)	−0.0561(7)	0.0520(6)	−0.1776(5)	4.4(3)
C(42)	−0.0034(7)	0.0847(6)	−0.1044(5)	5.3(4)
C(43)	0.0847(8)	0.0466(8)	−0.0753(5)	6.6(4)
C(44)	0.1145(9)	−0.0263(9)	−0.1205(7)	7.9(6)
C(45)	0.0591(9)	−0.0584(8)	−0.1928(7)	7.3(5)
C(46)	−0.0275(7)	−0.0201(6)	−0.2211(5)	6.0(4)
C(47)	−0.0322(8)	0.1643(7)	−0.0546(4)	6.0(4)
C(48)	−0.0897(8)	−0.0586(8)	−0.2994(5)	7.2(4)
C(51)	−0.0834(8)	0.2147(6)	−0.3947(5)	5.4(4)
C(52)	0.004(1)	0.1755(8)	−0.4062(6)	7.3(5)
C(53)	0.008(1)	0.138(1)	−0.4790(8)	10.1(7)
C(54)	−0.072(1)	0.140(1)	−0.5386(8)	11.5(8)
C(55)	−0.158(1)	0.184(1)	−0.5253(6)	10.1(7)
C(56)	−0.166(1)	0.2195(7)	−0.4542(5)	6.7(4)
C(57)	0.0927(9)	0.1731(9)	−0.3439(6)	8.2(5)
C(58)	−0.2581(9)	0.2647(8)	−0.4421(5)	7.3(5)
C(61)	−0.3267(7)	0.2126(6)	−0.0816(5)	4.9(4)
C(62)	−0.3436(7)	0.3056(7)	−0.0537(5)	5.5(4)
C(63)	−0.3897(8)	0.308(1)	0.0117(6)	7.3(5)
C(64)	−0.417(1)	0.219(1)	0.0488(6)	8.3(5)
C(65)	−0.3971(8)	0.1289(8)	0.0229(6)	7.4(5)
C(66)	−0.3521(7)	0.1243(7)	−0.0430(5)	5.7(4)
C(67)	−0.3100(9)	0.4018(7)	−0.0945(5)	7.2(4)
C(68)	−0.3332(8)	0.0238(7)	−0.0718(5)	6.9(4)

Table 5. Selected Bond Distances (Å) and Angles (deg) for [Na(THF)₃]₂[UO₂(O-2,6-Me₂C₆H₃)₄] (**4**)

U(1)−O(1)	1.816(5)	U(1)−O(2)	1.812(5)
U(1)−O(3)	2.217(5)	U(1)−O(4)	2.282(5)
U(1)−O(5)	2.294(5)	U(1)−O(6)	2.190(5)
Na(1)−O(2)	2.357(6)	Na(1)−O(7)	2.406(8)
Na(1)−O(8)	2.376(7)	Na(1)−O(9)	2.321(8)
Na(2)−O(1)	2.392(6)	Na(2)−O(4)	2.463(6)
Na(2)−O(10)	2.376(8)	Na(2)−O(11)	2.378(8)
Na(2)−O(12)	2.403(7)		
O(1)−U(1)−O(2)	175.5(2)	U(1)−O(2)−Na(1)	113.1(2)
O(1)−U(1)−O(4)	83.2(2)	U(1)−O(5)−Na(1)	93.9(2)
O(1)−U(1)−O(6)	89.8(2)	U(1)−O(3)−C(31)	159.7(5)
O(2)−U(1)−O(5)	83.2(2)	U(1)−O(4)−C(41)	142.6(5)
O(1)−U(1)−O(3)	92.3(2)	U(1)−O(5)−C(51)	140.5(5)
O(1)−U(1)−O(5)	94.1(2)	U(1)−O(6)−C(61)	167.6(5)
U(1)−O(1)−Na(2)	110.4(2)	O(1)−Na(2)−O(4)	68.8(2)
U(1)−O(4)−Na(2)	93.9(2)	O(2)−Na(1)−O(5)	69.2(2)

be described as distorted trigonal bipyramidal with O(2) and O(9) occupying axial positions in the case of Na(1) (O(2)−Na(1)−O(9) = 156.4(3)°) and O(1) and O(12) in the axial positions of Na(2) (O(1)−Na(2)−O(12) = 169.2(3)°). Within

the sodium cation environments, the longest Na−O distance in each case is exhibited by the oxygen atom within the aryloxide ligand (Na(1)−O(5) = 2.482(6) Å and Na(2)−O(4) = 2.463(6) Å). Uranyl oxygen−metal bond distances in **4**, at 1.812(5) and 1.816(5) Å, are somewhat lengthened in comparison with the majority of uranyl structures (normally 1.77−1.79 Å), which is most probably a reflection of the uranyl oxygen−sodium cation interactions. A systematic variation in U−O bond lengths to the aryloxide ligands is also discernible. The two aryloxide ligands which are not involved in coordination to the sodium cations (*i.e.* those containing O(6) and O(3)) exhibit U−O distances very similar to those in **3** (2.190(5) and 2.217(5) Å, respectively), while the aryloxide ligands containing O(4) and O(5) (which make Na−O interactions) exhibit significantly longer U−O distances of 2.282(5) and 2.294(5) Å, respectively. U−O−C bond angles within the aryloxide ligands also differ considerably depending upon whether the aryloxide oxygen atom is involved in coordination to the sodium cations. Thus the aryloxide ligands containing O(3) and O(6) exhibit obtuse U−O−C angles of 159.7(5) and 167.6(6)°, respectively, while those involved in sodium coordination (O(4) and O(5)) exhibit considerably more acute angles of 142.6(5) and 140.5(5)°.

Concluding Remarks

Metathesis reactions of uranyl chloride with alkali metal salts of the bis(trimethylsilyl)amido ion have been found to yield both neutral and anionic complexes, depending on the nature of the counterion. Reaction with the potassium salt results in the formation of the previously characterized complex UO$_2$[N(SiMe$_3$)$_2$]$_2$(THF)$_2$, while use of the sodium salt is found to produce the "ate" complex [Na(THF)$_2$]$_2$\{UO$_2$[N(SiMe$_3$)$_2$]$_4$\}. Isolation of complex salts is frequently found to accompany the use of salts of the lighter alkali metals in metathesis reactions, most likely as a result of the increased strength of dative M···O bond interactions. Both complexes serve as suitable precursors in alcoholysis reactions and permit isolation of the complexes UO$_2$(O-2,6-*i*-Pr$_2$C$_6$H$_3$)$_2$(py)$_3$ and [Na(THF)$_3$]$_2$-[UO$_2$(O-2,6-Me$_2$C$_6$H$_3$)$_4$], respectively. Structural studies reveal the presence of a significant lengthening of the U−O(uranyl) bond length upon coordination to a sodium counterion. This structural difference apparently has little effect on the U−O bond order, however, and no significant lowering of the U−O vibrations is observed. Further, base coordination and cation coordination do not provide stereochemical rigidity for these complexes in solution, and both of the aryloxide complexes exhibit fluxional behavior at room temperature.

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. Solvents, except for pyridine, were degassed and distilled from Na/benzophenone ketyl under nitrogen. Pyridine was distilled from CaH$_2$ under argon. 2,6-diisopropylphenol was purchased from Aldrich and distilled before use. 2,6-Dimethylphenol was purchased from Aldrich and used without further purification. Anhydrous uranyl chloride was prepared by heating uranium tetrachloride in a stream of oxygen at 325 °C. M[N(SiMe$_3$)$_2$] (M = Na, K) were prepared by refluxing HN(SiMe$_3$)$_2$ with NaH and KH, respectively, in toluene for 48 h. 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 a Vacuum Atmospheres glovebox, and a small amount was tested with a solution of sodium benzophenone in THF. Solvents that failed to maintain a purple coloration from this test were not used.

^{1}H NMR spectra were recorded on Brüker WM 300 or AF 250 spectrometers in benzene-d_6 or toluene-d_8. All ^{1}H NMR chemical shifts

are reported in ppm relative to the ^{1}H impurity in benzene-d_6 and toluene-d_8 set at δ 7.15 and 2.09, respectively. Infrared spectra were recorded on a Perkin-Elmer 1500 spectrophotometer interfaced with a 1502 central processor or on a BioRad FTS-40 spectrophotometer as Nujol mulls between KBr salt plates. Elemental analyses were performed in-house on a Perkin-Elmer 2400 CHN analyzer or by the Microanalytical facility at the University of California at Berkeley. In-house elemental analysis samples were prepared and sealed in tin capsules in the glovebox prior to combustion.

UO$_2$[N(SiMe$_3$)$_2$]$_2$(THF)$_2$ (1). To a stirred pale yellow slurry of 1.06 g (3.11 mmol) of UO$_2$Cl$_2$ in 75 mL of THF was added 1.57 g (5.76 mmol) of solid KN(SiMe$_3$)$_2$, producing a color change to orange. The solution was stirred at room temperature for 24 h and filtered through a Celite pad to give a clear orange filtrate. Solvent was removed *in vacuo*, and the residue was redissolved in 50 mL of 10:1 hexane/THF and placed at −40 °C. Orange crystals were deposited overnight, collected by filtration, and allowed to dry in the box atmosphere. Yield: 1.756 g (83%). ^{1}H NMR (benzene-d_6, 22 °C): δ 4.37 (br m, 2 H, α-THF), 1.50 (br m, 2 H, β-THF), 0.56 (s, 9 H, SiMe$_3$). IR (cm^{-1}): 1343 (w), 1251 (sh, s), 1240 (s), 1172 (w), 1073 (sh, w), 1052 (sh, m), 1022 (s), 943 (s), 922 (sh, m), 862 (s), 839 (s), 771 (s), 757 (s), 725 (sh, m), 682 (s), 661 (s), 608 (s). Anal. Calcd for C$_{20}$H$_{52}$N$_2$O$_4$-Si$_4$U: C, 32.68; H, 7.13; N, 3.81. Found: C, 32.84; H, 7.06; N, 4.48.

[Na(THF)$_2$]$_2$\{UO$_2$[N(SiMe$_3$)$_2$]$_4$\} (2). In the drybox, 0.50 g (1.47 mmol) of UO$_2$Cl$_2$ was slurried in 50 mL of THF and then 1.06 g (5.78 mmol) of solid NaN(SiMe$_3$)$_2$ added. The resulting orange solution was stirred overnight, filtered through a Celite pad, and reduced in volume. On standing in the freezer at −40 °C, large orange blocks were deposited. These were collected by filtration, and a second crop was obtained by adding hexane to the filtrate and cooling again. Total yield 1.70 g (93%). ^{1}H NMR (benzene-d_6, 22 °C): δ 3.20 (br m, 2 H, α-THF), 1.23 (br m, 2 H, β-THF), 0.68 (s, 9 H, SiMe$_3$). IR (cm^{-1}): 1253 (m), 1245 (sh, m), 1237 (m), 1045 (m), 956 (s), 889 (sh, w), 866 (sh, m), 858 (s), 841 (s), 771 (m), 753 (w), 736 (w), 721 (w), 686 (m), 661 (m), 608 (m), 456 (w). Anal. Calcd for C$_{40}$H$_{104}$N$_4$Na$_2$UO$_6$: C, 38.55; H, 8.43; N, 4.50; Na, 3.69. Found: C, 38.96; H, 8.16; N, 4.19; Na, 3.56.

UO$_2$(O-2,6-*i*-Pr$_2$C$_6$H$_3$)$_2$(py)$_3$ (3). To a solution of UO$_2$[N(SiMe$_3$)$_2$]$_2$-(THF)$_2$ (1) (0.70 g, 0.952 mmol) in toluene (75 mL) was added dropwise a solution of 0.34 g (1.91 mmol) of 2,6-diisopropylphenol in 10 mL of toluene, producing a color change from pale orange to a deep blood red. A 2 mL volume of pyridine was added and the mixture stirred at room temperature for 1 h. Solvent was removed *in vacuo* to leave a dark red solid residue. This was dissolved in 50 mL of toluene, and the mixture was filtered through a Celite pad. The volume of the filtrate was reduced to *ca.* 10 mL and then layered with 10 mL of hexane before being placed at −40 °C. Dark red crystals were deposited over a period of 2 days. These were collected by filtration and allowed to dry. Yield: 0.45 g (55%). ^{1}H NMR (benzene-d_6, 22 °C): δ 8.97 (d, $^3J_{HH}$ = 5 Hz, 6 H, *ortho*-py), 7.40 (d, $^3J_{HH}$ = 7 Hz, 4 H, *meta*-OAr), 6.85 (m, 5 H, *para*-py and *para*-OAr), 6.63 (m, 6 H, *meta*-py), 4.46 (septet, $^3J_{HH}$ = 7 Hz, 4 H, C*H*Me$_2$), 1.26 (d, $^3J_{HH}$ = 7 Hz, 24 H, CH*Me*$_2$). IR (cm^{-1}): 1630 (w), 1597 (s), 1584 (m), 1574 (sh, w), 1482 (sh, w), 1443 (s), 1430 (s), 1357 (m), 1336 (s), 1264 (s), 1211 (m), 1151 (m), 1107 (w), 1098 (m), 1067 (m), 1037 (m), 1007 (m), 934 (w), 875 (s), 857 (s), 797 (w), 789 (m), 751 (s), 727 (w), 700 (s), 623 (m), 564 (m), 556 (sh, m), 420 (w). Anal. Calcd for C$_{39}$H$_{49}$N$_3$O$_4$U: C, 54.35; H, 5.73; N, 4.88. Found: C, 54.53; H, 5.16; N, 5.07.

[Na(THF)$_3$]$_2$[UO$_2$(O-2,6-Me$_2$C$_6$H$_3$)$_4$] (4). To a stirred THF solution of [Na(THF)$_2$]$_2$\{UO$_2$[N(SiMe$_3$)$_2$]$_4$\} (2) (0.53 g, 0.43 mmol) was added 0.21 g (1.72 mmol) of 2,6-dimethylphenol as a solution in THF. The resulting mixture was stirred for 5 h before being concentrated and placed in the freezer at −40 °C. A dark red-brown crystalline solid was deposited, which was isolated by filtration (and was noted to tend to melt when isolated from THF). Addition of hexane to the filtrate and re-cooling produced a second crop of crystals. Total yield: 0.33 g (63%). ^{1}H NMR (benzene-d_6, 22 °C): δ 6.94 (d, 8 H, *meta* OAr), 6.32 (t, 4 H, *para* OAr), 3.58 (m, 24 H, α-THF), 2.56 (s, 24 H, Me), 1.73 (m, 24 H, β-THF). IR (cm^{-1}): 1589 (m), 1421 (m), 1268 (s), 1232 (s), 1221 (s), 1184 (m), 1089 (m), 1048 (m), 982 (w), 916 (w), 878 (s), 854 (s), 839 (m), 757 (m), 738 (m), 704 (m), 681 (w), 559

(w), 537 (m). Anal. Calcd for [Na(THF)$_3$]$_2$[UO$_2$(O-2,6-Me$_2$C$_6$H$_3$)$_4$]: C, 54.54; H, 6.87; Na, 3.73. Calcd for [Na(THF)]$_2$[UO$_2$(O-2,6-Me$_2$-C$_6$H$_3$)$_4$]: C, 50.84; H, 5.55; Na, 4.86. Found: C, 49.6; H, 5.80; Na, 3.97.

Crystallographic Studies. UO$_2$(O-2,6-*i*-Pr$_2$C$_6$H$_3$)$_2$(py)$_3$ (3). The crystals were examined in mineral oil under an argon stream, and a suitable crystal was mounted on a glass fiber with Apiezon grease and transferred to the −70 °C coldstream of an Enraf-Nonius CAD4 diffractometer. The crystals were dark red, and a plate of thickness 0.15 mm by 0.30 mm square was used with a long axis parallel to the fiber. A total of 24 reflections in the 2θ range 28−36° were used to determine an orientation matrix. A series of high-χ reflections were scanned to provide the basis for an empirical absorption correction. Data reduction was carried out using the Enraf-Nonius Structural Determination Package. All data were corrected for Lorentz and polarization effects and equivalent data averaged to a unique set of intensities and associated σ's in the usual manner. The uranium atom was located using direct methods, and all other non-hydrogen atoms were located from successive difference Fourier maps and refined by full-matrix least squares. Some of the isopropyl carbon atoms showed slightly high temperature factors, but no attempt was made to introduce a disordered model to account for this. All hydrogen atoms were introduced in calculated positions. Final refinement using 3183 unique observed [$F > 4\sigma(F)$] reflections converged at $R = 0.022$ and $R_w = 0.029$ {where $w = [\sigma^2(F) + 0.0007(F)^2]^{-1}$}. All data refinement calculations were performed using the SHELXTL PLUS suite of computer programs (Siemens Analytical X-ray Instruments, Inc., 1990).

[Na(THF)$_3$]$_2$[UO$_2$(O-2,6-Me$_2$C$_6$H$_3$)$_4$] (4). A dark red-brown block of dimensions 0.22 × 0.38 × 0.49 mm was mounted on a glass fiber using Apiezon grease and transferred to the −70 °C coldstream of an Enraf-Nonius CAD4 diffractometer. The structure was solved using the TEXRAY software package. After correction for decay and absorption (application of an empirical absorption correction based on ψ scans), redundant data were deleted (a sorting error precluded averaging of the data). The uranium atom was found using a Patterson map. Although the Wilson statistics made the structure look distinctly acentric, the compound refined satisfactorily only in the centric space group $P\bar{1}$. The remaining atoms were found by standard Fourier techniques. All non-hydrogen atoms were refined anisotropically. The final difference Fourier map did not reveal the hydrogen atom positions, and so they were not included in the structure. Attempted refinement of the secondary extinction coefficient resulted in a negative value, and so the parameter was not included in later least-squares cycles. The largest peak in the final difference Fourier map was approximately equidistant from O(11), C(111), C(112), C(113), and C(114). The data were refined on F_o.

Supporting Information Available: Tables of complete fractional coordinates and isotropic thermal parameters, bond distances, bond angles, and anisotropic thermal parameters for **3** and **4** (19 pages). Ordering information is given on any current masthead page.

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