Alkoxide and Aryloxide Derivatives of a (Triamidoamine)uranium Complex

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The (triamidoamine)uranium chloride complex $[\{U(NN_3)(\mu\text{-Cl})\}_2]$ $[NN_3 = N(CH_2CH_2NSiMe_3)_3]$ reacts with alkali metal alkoxides and aryloxides to give a range of complexes $[U(NN_3)(OR)]$ (R = Bu^t, *t*-C_4F_9, Ph, 2,6-Bu^t_2-4-MeC_6H_2). Crystallographic investigations (including the molecular structure of the perfluoro-*tert*-butoxido derivative $[U(NN_3)(O\text{-}t\text{-}C_4F_9)]$), molecular weight determinations, and NMR spectroscopic data are consistent with these molecules being monomeric with a 3-fold symmetric arrangement of the triamidoamine fragment. The three turquoise *ate* complexes $[U(NN_3)(OR)(OR')Li(THF)_n]$ (R, R′ = Bu^t or Ph), are prepared by reaction of the corresponding uranium alkoxides with lithium phenoxide or *tert*-butoxide. The complex with R = Ph, R′ = Bu^t, $n = 1$ is shown by X-ray crystallography to have a capped trigonal bipyramidal structure. A lithium atom is incorporated into the ligand sphere by coordination to an amido nitrogen and a *tert*-butoxido oxygen. The mixed alkoxide *ate* complex $[U(NN_3)(OBu^t)(OPh)Li(THF)]$ gives only $[U(NN_3)(OBu^t)]$ on heating *in vacuo*. The one-electron oxidation of these *ate* complexes to the three neutral pentavalent compounds $[U(NN_3)(OR)(OR')]$ (R, R′ = Bu^t or Ph) has been characterized by cyclic voltammetric studies and performed on the chemical scale by reaction with $[FeCp_2][PF_6]$.

Introduction

Substituted triamido amine ligands, derived from tris(aminoethyl)amine (TREN), have been used in the synthesis of a wide range of novel complexes of main group[3] and transition elements.[4] In the majority of such compounds containing one metal atom, the (triamidoamine)metal or azametallatrane fragment has approximate trigonal monopyramidal geometry, leaving one axial coordination site at the metal. We have found that in tetravalent actinide complexes of this class, the trimethylsilyl-substituted ligand is often distorted from 3-fold symmetry; the complex $[\{(NN_3)U(\mu\text{-Cl})\}_2]$ for example consists of two edge-sharing octahedra.[5] Presumably this occurs as a consequence of the large size of uranium and thorium. Nevertheless, the chelate (triamidoamine)actinide fragment is quite robust, tolerating substitution reactions in the auxiliary coordination sphere and allowing the isolation of unique classes of compounds.[6,7] Here we report the synthesis of a range of 3-fold-symmetric alkoxide and aryloxide derivatives of this system, isolation of bis(alkoxido) *ate* complexes, and the subsequent electrochemical synthesis of U(V) alkoxides.

Experimental Section

All manipulations were carried out under an inert atmosphere of argon either with standard Schlenk techniques or in an MBraun drybox. NMR samples were prepared in the drybox, and the sample tubes were sealed *in vacuo* or by using Young's type concentric stopcocks. Solvents were predried over sodium wire and then distilled over potassium (tetrahydrofuran), sodium (toluene), or sodium−potassium alloy (pentane) under an atmosphere of nitrogen. Deuterated solvents were dried over molten potassium and distilled. NMR spectra were recorded on a Bruker WM-360 or DMX-300 spectrometer, and the spectra were referenced internally using residual protio solvent resonances relative to tetramethylsilane ($\delta = 0$ ppm). Infrared spectra were obtained as Nujol mulls in an airtight holder using a Perkin-Elmer FTIR spectrometer. EI mass spectra were obtained on a VG Autospec mass spectrometer by Dr. Ali Abdul-Sada. Elemental analyses were performed by Canadian Microanalytical Services Ltd., Delta, BC, Canada. Cryoscopic solution molecular weight determinations were performed on *ca.* 200 mg samples in cyclohexane.[8] Literature methods were used for the preparation of $[Li_3(NN_3)]$[9] and $[\{U(NN_3)(\mu\text{-Cl})\}_2]$.[5] $K[OBu^t]$ and $[FeCp_2]PF_6$ were purchased from Aldrich Chemical Co. Ltd. and dried at 100 °C *in vacuo* for a few hours before use. [Li(OPh)] and $[Li(OC_6H_2Bu_2Me)]$ were prepared by addition of stoichiometric amounts of lithium butyl to toluene solutions of the pure phenols and drying of the precipitated white solids *in vacuo*.

$[U\{N(CH_2CH_2NSiMe_2Bu^t)_3\}(OBu^t)]$, 4. Tetrahydrofuran (20 cm^3) was added at −80 °C to a mixture of $[U\{N(CH_2CH_2NSiMe_2Bu^t)_3\}Cl]$ (0.25 g, 0.30 mmol) and $[K(OBu^t)]$ (0.037 g, 0.30 mmol). The mixture was stirred for 12 h at ambient temperature to give a light purple solution. After evaporation of volatiles, the residue was sublimed at 180 °C and 10^{-6} mbar to give an analytically pure light purple solid (0.17 g, 65%). Anal. Calc for $C_{28}H_{66}N_4OSi_3U$: C, 41.53; H, 8.33; N, 6.95. Found: C, 42.19; H, 8.34; N, 7.03. ^1H NMR (C_6D_6): δ 79.96

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(s, 6H, CH_2), 61.96 (s, 9H, OBu^t), 10.94 (s, 6H, CH_2), −16.19 (s, 24H, Bu^t), −36.46 (s, 18H, Me_2Si). MS (EI): *m/z* 796 (32%, M^+), 740 (14%, M − Bu^t). IR (Nujol), cm^{-1}: 1143m, 1075s, 1060s, 1024m, 1006m, 968s, 927s, 896m, 803s, 739s. UV λ_{max}, nm (ϵ, M^{-1} cm^{-1}): 501 (45), 520 (47), 559 (26), 607 (22), 659 (27), 698 (47), 715 (29) 810 (17).

[U(NN$_3$)(O-*t*-C$_4$F$_9$)], 5. Tetrahydrofuran (20 cm^3) was added at −80 °C to a mixture of [{U(NN$_3$)Cl}$_2$] (0.20 g, 0.16 mmol) and [K(O-*t*-C_4F_9)] (0.087 g, 0.32 mmol). The mixture was stirred for 8 h at ambient temperature to give a pale green solution. After evaporation of volatiles, the residue was sublimed at 100 °C and 10^{-6} mbar to give an analytically pure pale green solid (0.216 g, 81%), which was recrystallized from pentane at −50 °C to give transparent needles suitable for X-ray diffraction. Anal. Calc for $C_{19}H_{39}N_4OF_9Si_3U$: C, 26.67; H, 4.77; N, 6.36. Found: C, 27.40; H, 4.72; N, 6.73. ^1H NMR (C_6D_6): δ 3.57 (6H, s, CH_2), −1.39 (6H, s, CH_2), −7.43 (27H, s, $SiMe_3$). $^{19}F\{^1H\}$ NMR (C_6D_6): δ −2.30 (s, CF_3). MS (EI): *m/z* 832 (51%, M^+), 599 (100%, M − OC_4F_9). IR (Nujol), cm^{-1}: 1142w, 1071m, 1024w, 971s, 925m, 897w, 838s, 768m, 743w, 726m. UV λ_{max}, nm (ϵ, M^{-1} cm^{-1}): 523 (58), 676 (31), 705 (30). Solution molecular weight (C_6H_{12}): 805.

[U(NN$_3$)(OPh)], 6. Tetrahydrofuran (20 cm^3) was added at −80 °C to a mixture of [{U(NN$_3$)Cl}$_2$] (0.20 g, 0.16 mmol) and [Li(OPh)] (0.032 g, 0.32 mmol), and the resulting mixture was stirred for 8 h at ambient temperature to give a green solution. After evaporation of volatiles, the residue was sublimed at 150 °C and 10^{-6} mbar to give an analytically pure green solid (0.117 g, 53%). Anal. Calc for $C_{21}H_{44}N_4OSi_3U$: C, 36.09; H, 6.31; N, 8.00. Found: C, 36.51; H, 6.42; N, 8.11. ^1H NMR (C_6D_6): δ 40.11 (2H, s, CH), 21.60 (2H, s, CH), 19.78 (6H, s, CH_2), 17.54 (1H, t, *para*-CH), 16.94 (6H, s, CH_2), −15.16 (27H, s, $SiMe_3$). MS (EI): *m/z* 690 (100%, M^+), 599 (78%, M − OC_6H_5). IR (Nujol), cm^{-1}: 1141w, 1079m, 998w, 927m, 881w, 837s, 769m, 756m, 743w, 722m. UV λ_{max}, nm (ϵ, M^{-1} cm^{-1}): 669 (33), 709 (45). Solution molecular weight (C_6H_{12}): 600.

[U(NN$_3$)(O-2,6-Bu$^t_2$-4-MeC$_6$H$_2$)], 7. Tetrahydrofuran (20 cm^3) was added at −80 °C to a mixture of [{U(NN$_3$)Cl}$_2$] (0.20 g, 0.16 mmol) and [Li(O-2,6-Bu^t_2-4-MeC_6H_2)] (0.072 g, 0.32 mmol). The mixture was stirred for 8 h at ambient temperature to give a light green solution. After evaporation of volatiles, the residue was distilled at 190 °C and 10^{-6} mbar to give an analytically pure green oil which solidified upon cooling (0.20 g, 77%). Anal. Calc for $C_{30}H_{62}N_4OSi_3U$: C, 42.87; H, 7.66; N, 6.92. Found: C, 44.10; H, 7.65; N, 6.86. ^1H NMR (C_6D_6): δ 27.09 (2H, s, CH), 25.29 (6H, s, CH_2), 13.21 (3H, s, Me), 5.84 (18H, s, Bu^t), 2.16 (6H, s, CH_2), −15.35 (27H, s, $SiMe_3$). MS (EI): *m/z* 817 (33%, M^+), 599 (100%, M − OAr*). IR (Nujol), cm^{-1}: 1145w, 1119m, 1073s, 1028w, 931s, 903m, 836s, 800m, 772m, 723m. UV λ_{max}, nm (ϵ, M^{-1} cm^{-1}): 520 (78), 538 (71), 607 (49), 681 (40). Solution molecular weight (C_6H_{12}): 800.

[U(NN$_3$)(OPh)$_2$Li(THF)$_2$], 8. Tetrahydrofuran (20 cm^3) was added at −80 °C to a mixture of [{U(NN$_3$)Cl}$_2$] (0.20 g, 0.16 mmol) and [Li(OPh)] (0.064 g, 0.64 mmol), and the resulting mixture was stirred for 8 h at ambient temperature to give a turquoise solution. After evaporation of volatiles, the residue was extracted with pentane (10 cm^3), and the extract was filtered. Crystallization at 0 °C gave blue-green elongated cubes (0.164 g, 55%). Anal. Calc for $C_{35}H_{65}N_4O_4Si_3ULi$: C, 43.95; H, 6.72; N, 5.88. Found: C, 44.95; H, 7.01; N, 5.99. ^1H NMR (C_6D_6): δ 46.29 (s, 4H), 22.16 (s, 4H), 11.78 (br s, 5H), 1.26 (s, 2H), −4.47 (s, 28H), −7.26 (s, 2H), −22.82 (br s, 5H). $^7Li\{^1H\}$ NMR (C_6D_6): δ 57.63 (s). MS (EI): *m/z* 784 (3%, M − Li(THF)$_2$), 690 (63%, M − OPhLi(THF)$_2$), 599 (8%, M − O_2Ph_2Li(THF)$_2$). IR (Nujol), cm^{-1}: 1594s, 1071w, 1023w, 994m, 957w, 882m, 824m, 764s, 722m, 699s. UV λ_{max}, nm (ϵ, M^{-1} cm^{-1}): 538 (38), 581 (40), 663 (35), 704 (32), 890 (8).

[U(NN$_3$)(OPh)(OBu^t)Li(THF)], 9. Tetrahydrofuran (20 cm^3) was added at 25 °C to a mixture of freshly sublimed [U(NN$_3$)(OPh)] (0.40 g, 0.60 mmol) and [Li(OBu^t)] (0.047 g, 0.60 mmol). The mixture was stirred for 3 h to give a turquoise solution. After evaporation of volatiles, the residue was extracted into pentane (10 cm^3), and the extract was filtered. Cooling to −30 °C gave blue-green elongated cubes suitable for X-ray diffraction (0.313 g, 59%). Anal. Calc for $C_{29}H_{61}N_4O_3Si_3ULi$: C, 40.35; H, 7.01; N, 5.91. Found: C, 41.35; H, 7.29; N, 6.65. ^1H NMR (C_6D_6): δ 62.72 (s, 2H), 57.40 (s, 1.5H), 40.23 (br s, 2H), 9.83 (s, 1H), 7.92 (br s, 2H), 3.35 (s, 2H), −9.85 (br s, 9H), −28.08 (s, 4.5H). $^7Li\{^1H\}$ NMR (C_6D_6): δ 69.65 (s). MS (EI): *m/z* 690 (31%, M − OBu^tLiTHF), 670 (100%, M − OPhLiTHF), 597 (33%, M − OPhOBu^tLiTHF). IR (Nujol), cm^{-1}: 1591s, 1580s, 1190s, 1160s, 1148m, 1061s, 1033s, 995m, 933s, 837s, 762s, 724s. UV λ_{max}, nm (ϵ, M^{-1} cm^{-1}): 661 (34), 702 (32), 716 (27).

[U(NN$_3$)(OBu^t)$_2$Li(THF)], 10. Tetrahydrofuran (20 cm^3) was added at −80 °C to a mixture of [{U(NN$_3$)Cl}$_2$] (0.20 g, 0.16 mmol) and [Li(OBu^t)] (0.050 g, 0.64 mmol). The mixture was stirred for 8 h at ambient temperature to give a turquoise solution. After evaporation of volatiles, the residue was extracted into pentane (10 cm^3), and the extract was filtered. Cooling to −30 °C gave blue-green cubes (0.148 g, 57%). Anal. Calc for $C_{27}H_{65}N_4O_3Si_3ULi$: C, 36.79; H, 7.65; N, 6.66. Found: C, 37.19; H, 7.85; N, 7.46. ^1H NMR (C_6D_6): δ 53.20 (s, 6H, CH_2), 49.63 (s, 9H, OBu^t), 9.62 (s, 6H, CH_2), 6.88 (s, 16H, thf), 3.08 (s, 16H, THF), 1.55 (s, 9H, (OBu^t), −24.90 (s, 27H, Me_3Si). ^7Li NMR (C_6D_6): δ 79.16 (s). MS (EI): *m/z* 670 (24%, M − OBu^tLiTHF), 597 (100%, M − $O_2Bu^t_2$LiTHF). IR (Nujol), cm^{-1}: 1186m, 1150w, 1086m, 1054m, 1037m, 970s, 930s, 832s, 766m, 738m. UV λ_{max}, nm (ϵ, M^{-1} cm^{-1}): 702 (26), 716 (21).

[U(NN$_3$)(OPh)$_2$], 11. Pentane (10 cm^3) was added at 25 °C to a mixture of **8** (0.30 g, 0.40 mmol) and [$FeCp_2$]PF_6 (0.107 g, 0.30 mmol). The mixture was stirred for 2 h to give a brown solution. After evaporation of volatiles and sublimation of the ferrocene coproduct onto a liquid-nitrogen-cooled probe, the residue was extracted into pentane (5 cm^3), the extract was filtered, and the filtrate was cooled to −30 °C to give a dark brown solid (0.194 g, 77%). Anal. Calc for $C_{27}H_{49}N_4O_2Si_3U$: C, 40.29; H, 6.07; N, 6.98. Found: C, 41.36; H, 6.30; N, 7.15. ^1H NMR (C_6D_6): δ 16.77 (br s, 6H, CH_2), 10.70 (br s, 4H, CH), 9.73 (s, 4H, CH), 8.15 (br s, 6H, CH_2), 7.41 (s, 2H, *para*-CH), −2.92 (s, 27H, $SiMe_3$). MS (EI): *m/z* 783 (22%, M^+), 690 (79%, M − OPh), 597 (50%, M − O_2Ph_2). IR (Nujol), cm^{-1}: 1138w, 1057s, 1019w, 997w, 936s, 918s, 899s, 840s, 770s, 755s, 722s. UV: no peaks observed in the range 300−900 nm.

[U(NN$_3$)(OPh)(OBu^t)], 12. This complex was prepared similarly to **11** as a dark brown solid (69%). Anal. Calc for $C_{25}H_{53}N_4O_2Si_3U$: C, 39.16; H, 6.80; N, 7.02. Found: C, 39.30; H, 6.99; N, 7.33. ^1H NMR (C_6D_6): δ 11.59 (br s, 2H), 10.30 (s, 2H), 8.30 (s, 1H), 7.41 (br s, 6H), −4.33 (br s, 30H). MS (EI): *m/z* 763 (13%, M^+), 690 (34%, M − OBu^t), 670 (9%, M − OPh), 597 (60%, M − OBu^tOPh). IR (Nujol), cm^{-1}: 1161m, 1108m, 1079m, 1056m, 1020m, 1005m, 951s, 934s, 904s, 894s, 871s, 837s, 816s. UV: no peaks observed in the range 300−900 nm.

[U(NN$_3$)(OBu^t)$_2$], 13. This complex was prepared similarly to **11** as a dark brown solid (51%). Anal. Calc for $C_{23}H_{57}N_4O_2Si_3U$: C, 36.07; H, 7.57; N, 7.47. Found: C, 37.13; H, 7.72; N, 7.53. ^1H NMR (C_6D_6): δ 31 (br s, 6H, CH_2), 27 (br s, 6H, CH_2), 9.25 (br s, 9H, OBu^t), 4.74 (br s, 9H, OBu^t), −3.42 (4 peaks overlapping br s, 27H, Me_3Si). MS (EI): *m/z* 743 (9%, M^+), 670 (32%, M − OBu^t), 597 (100%, M − $O_2Bu^t_2$). IR (Nujol), cm^{-1}: 1142m, 1108s, 1055s, 1018s, 888s, 681m. UV: no peaks observed in the range 300−900 nm.

Crystallography. Crystals of **5** and **9** were coated with inert oil and transferred to the cold (173 K) N_2 gas stream on the diffractometer (Enraf-Nonius CAD4). Non-H atoms were located by heavy-atom methods (SHELXS-86) and refined by full-matrix least-squares procedures on all F^2 with anisotropic thermal parameters (SHELXL-93)[10] and scattering factors from ref 11. . C(19) in **5** became nonpositive definite and was reset isotropic. H atoms were included in the riding mode with $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}(C)$ for methyl groups. Table 1 lists full experimental data.

Cyclic Voltammetry. Cyclic voltammetry was performed using an ADInstuments MacLab potentiostat and interface running EChem software, and the data were processed using Igor Pro software. The single-compartment airtight cell comprised a Pt disk working electrode, Pt wire auxiliary electrode, and Ag wire pseudoreference electrode; 0.1 M tetrabutylammonium hexafluorophosphate in THF was used as

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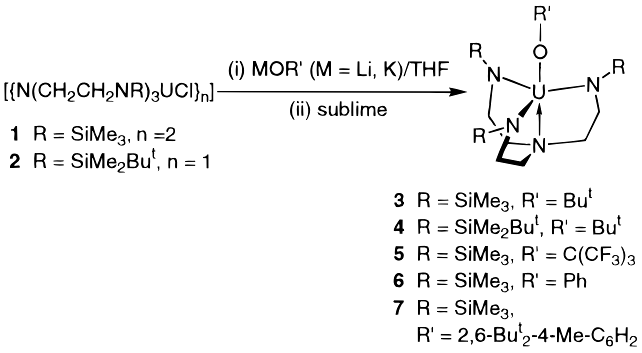
Table 1. Experimental Data for the X-ray Diffraction Study of **5** and **9**[a]

	5	**9**
mol formula	$C_{19}H_{39}F_9N_4OSi_3U$	$C_{29}H_{61}LiN_4O_3Si_3U$
formula weight	832.84	843.1
crystal system	monoclinic	orthorhombic
space group	$P2_1/n$ (nonstandard No. 14)	$P2_12_12_1$ (No. 19)
a/Å	12.009(4)	10.812(4)
b/Å	21.713(5)	18.567(5)
c/Å	12.125(3)	19.316(7)
β/deg	92.44(2)	90
cell vol/Å^3	3159(2)	3878(2)
Z	4	4
density (calcd)/g cm^{-3}	1.75	1.44
F(000)	1616	1696
λ(Mo Kα)/Å	0.710 73	0.710 73
μ/mm^{-1}	5.33	4.31
temp/K	173(2)	173(2)
crystal size/mm	0.30 × 0.20 × 0.10	0.40 × 0.40 × 0.35
θ_{max}/deg	25	25
no. of independent reflns	5555 [$R_{int} = 0.0650$]	3713 [$R_{int} = 0.0000$]
no. of significant reflns, $I > 2\sigma(I)$	3697	2728
no. of params	334	366
empirical abs cor: T_{max}, T_{min}	0.99, 0.79 (from ψ scans)	1.00, 0.78
goodness of fit on F^2	1.006	1.059
$\Delta\rho$/e Å^{-3}: max, min	+1.71, −1.40 (near U)	1.67, −1.36 (near U)
shift/esd max	0.001	0.002
$R_1[I > 2\sigma(I)]$, wR_2(all data)	0.064, 0.183	0.048, 0.103
a, b	0.1, 0	0.038, 0

[a] Details in common: scan mode $\omega-2\theta$; weighting scheme $w = 1/[\sigma^2(F^2) + (aP)^2 + bP]$ where P is $^1/_3$[maximum of (θ or F^2)] + $^2/_3F^2$.

Scheme 1. Synthesis of $[U(NN_3)(OR)]$ Complexes



the electrolyte. Potentials were calibrated by the method of Gagné[12] and are quoted versus the potential of the ferrocenium/ferrocene couple. No compensation for the resistance of the cell was applied.

Results and Discussion

Synthesis of Neutral Alkoxide and Aryloxide Derivatives 3−7. The *tert*-butoxido derivative $[U(NN_3)(OBu^t)]$, **3**, was prepared *via* reaction of the dimeric chloro complex $[\{U(NN_3)(\mu\text{-}Cl)\}_2]$[5] with $[K(OBu^t)]$ (Scheme 1). This pale pink/purple material is very soluble in pentane and, while extremely air and water sensitive, is thermally robust. When a sealed glass tube containing presublimed **3** was heated to *ca*. 60 °C, large clear crystals slowly formed. Partial solution of the X-ray crystallographic data obtained from these crystals[13] and the cryoscopic molecular weight are consistent with **3** being 3-fold symmetric and monomeric. Since all our previous tris(trimethylsilyl)-triamidoamine complexes of the actinides had displayed less symmetric structures than that proposed for **3**, we set out to find related derivatives which might yield fully soluble crystallographic data.

First, we examined the effect of variation of substituent groups on the triamidoamine ligand. Reaction of the monomeric tris(*tert*-butyldimethylsilyl) substituted compound $[\{N(CH_2CH_2NSiMe_2Bu^t)_3\}UCl]$, **2**,[7] with potassium *tert*-butoxide in pentane gave a purple-brown solution and, after evaporation and sublimation of the residue at 180 °C and 10^{-6} mbar, yielded pink crystals of monomeric $[\{N(CH_2CH_2NSiMe_2Bu^t)_3\}U(OBu^t)]$, **4**, in 65% yield. Single crystals of this compound grown from pentane solution gave reasonably good quality X-ray diffraction data, but solution was precluded as with **3**.

We further envisaged that substitution of the *tert*-butoxido group in **3** with perfluoro-*tert*-butoxido would lead to a change in the bond lengths around the metal atom and thus a lowering of the problematic symmetry of the molecule. Accordingly, reaction of **1** with stoichiometric amounts of $[K(O\text{-}t\text{-}C_4F_9)]$[14] followed by sublimation and recrystallization of the product from pentane gave crystals of the target complex $[U(NN_3)(O\text{-}t\text{-}C_4F_9)]$, **5**. Complete solution of the X-ray diffraction data for **5** was possible, and the molecular structure is shown in Figure 1. Selected bond lengths and angles are given in Table 2. No other structurally characterized perfluoroalkyl complexes of uranium(IV) have appeared, although the structure of pentavalent $[U(O\text{-}t\text{-}C_4F_9)_4(OEt)(HOEt)]$ is known.[15] The triamidoamine fragment in **5** is disposed with approximate 3-fold symmetry about the U atom in a manner similar to that usually observed for the smaller transition and main group elements. The U atom sits *ca*. 0.78 Å out of the plane defined by the three amido nitrogen atoms N(2), N(3), and N(4). The apex N(1)−U distance of 2.624(11) Å is rather larger than the typical value of 2.2−2.3 Å for the molybdenum(IV) derivatives with this structure type, consistent with the larger radius of U(IV). The C(16)−O(1) distance of 1.43(2) Å is essentially identical

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(12) Gagné, R. R.; Koval, C. A.; Lisensky, G. C. *Inorg. Chem.* **1980**, *19*, 2854.

(13) Two independent molecules with approximate C_{3v} symmetry were located in the unit cell [trigonal ($P3$), $a = b = 12.006(7)$ Å, $c = 11.699(8)$ Å]. Complete solution of the data set was impeded by the coincidence of the U atom with the plane formed by the three Si atoms and the consequent formation of a pseudomirror plane. This phenomenon has severely hampered our efforts to solve a number of other data sets incorporating 3-fold symmetric (triamidoamine)U fragments.

(14) Dear, R. E. A.; Fox, W. B.; Fredericks, R. J.; Gilbert, E. E.; Huggins, D. K. *Inorg. Chem.* **1970**, *11*, 2590.

(15) Larson, E. M.; Ella, P. G.; Larson, A. C. *Lanthanide Actinide Res.* **1986**, *1*, 307.

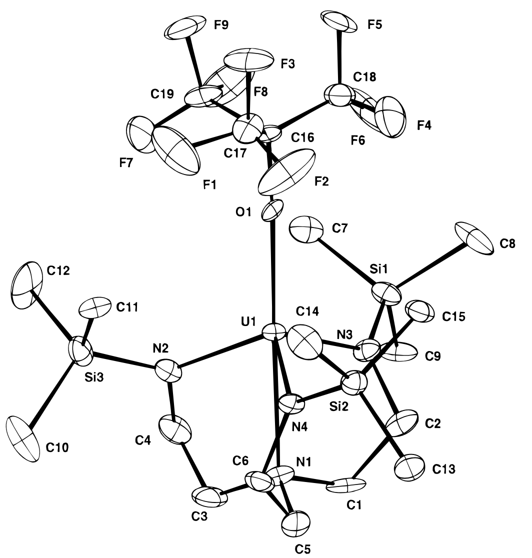


Figure 1. Thermal ellipsoid plot of the molecular structure of **5**. Hydrogen atoms are omitted.

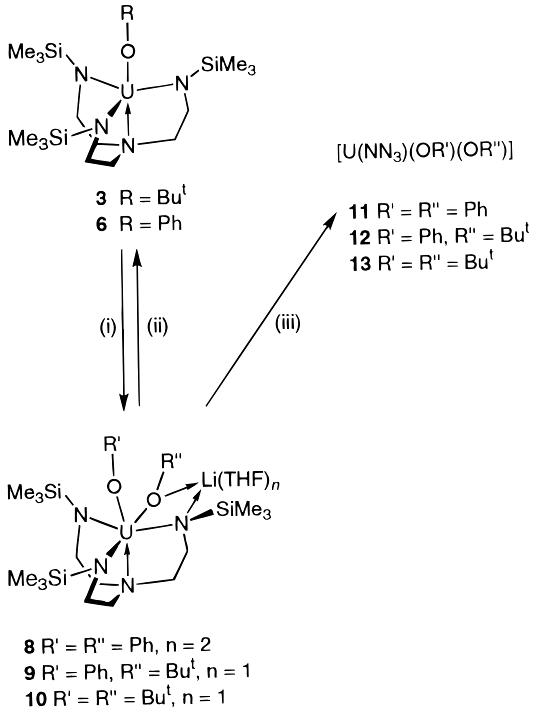
Table 2. Selected Bond Lengths (Å) and Angles (deg) for **5**

U(1)−O(1)	2.208(9)	Si(1)−N(3)	1.725(12)
U(1)−N(4)	2.210(11)	Si(2)−N(4)	1.730(12)
U(1)−N(3)	2.214(11)	Si(3)−N(2)	1.735(13)
U(1)−N(2)	2.222(12)	O(1)−C(16)	1.43(2)
U(1)−N(1)	2.624(11)		
O(1)−U(1)−N(4)	112.3(4)	O(1)−U(1)−N(1)	177.9(3)
O(1)−U(1)−N(3)	107.2(4)	C(16)−O(1)−U(1)	173.7(9)
O(1)−U(1)−N(2)	112.7(4)		

to that of 1.43(2) Å in [$UCp_3\{OC(CF_3)_2CCl_3\}$].[16] The U(1)−O(1) distance of 2.208(9) Å is similar to the 2.23(1) Å in the latter compound but is considerably longer than those in a range of (*tert*-butoxido)uranium(IV) compounds (*ca.* 2.10 Å).[17] This presumably arises from the expected contraction of the lone pairs on oxygen on moving to the more electron-withdrawing substituent and concomitant reduction in contribution from O−U π-bonding. The slight bend in C(16)−O(1)−U(1) [173.7(9)°] directs the bulky perfluoro-*tert*-butoxido group toward the less crowded space between two trimethylsilyl substituents.

We were interested in assessing the importance of size of the alkoxide groups in determining the nuclearity of this type of complex. The reaction of **1** with a 2-fold excess of lithium phenoxide in THF gave rise to the formation of a blue-green solution (*vide infra*). Evaporation of the solvent and distillation of the residue at 140 °C and 10^{-6} mbar gave pure pale green oily [$U(NN_3)(OPh)$], **6**, which slowly solidified. The ^1H NMR spectrum of this material[18] gave three well-resolved peaks for the aromatic C−H groups. Mass spectra of **6** gave no significant peaks of higher *m/z* than that expected for a monomeric species, and the solution molecular weight was close to that expected. While we have been unable to isolate homogeneous samples of alkoxide derivatives with groups less sterically demanding than phenyl, the bulky aryloxido derivative [$U(NN_3)(O\text{-}2,6\text{-}Bu^t_2\text{-}4\text{-}MeC_6H_2)$], **7**, was prepared by reaction of [$Li(O\text{-}2,6\text{-}Bu^t_2\text{-}4\text{-}MeC_6H_2)$] with **1** and has spectroscopic properties similar to those of the unsubstituted analogue **6**.

Scheme 2[a]



[a] Key: (i) Li[OPh] or Li[OBu^t]/THF; (ii) sublime *in vacuo*; (iii) [$FeCp_2$]PF_6 in pentane.

Synthesis of the *ate* Complexes [$U(NN_3)(OR)(OR')Li(THF)_n$]. We had noticed that reaction of green **1** with [Li(OPh)] in THF gave rise to the formation of a blue-green solution (*vide supra*). Evaporation of solvent *in vacuo* and crystallization of the residue from pentane gave blue-green [$U(NN_3)(OPh)_2Li(THF)_2$], **8** (Scheme 2). We were unable to assign the ^1H NMR spectrum completely. The mass spectrum was similar to that of the neutral phenoxide **6** but with an additional peak assignable to the fragment [$U(NN_3)(OPh)_2$]. A full solution of the X-ray crystal structure of **8** was prevented by rapid desolvation of the crystals.

Unsurprisingly, no complex salt intermediates could be detected in the syntheses of **3** and **5** when potassium alkoxides were used; *ate* complexes incorporating the later group 1 elements are considerably more labile than those of lithium. In the cases of **4** and **7**, incorporation of a second alkoxido ligand is prevented by steric bulk. We were pleased to find, however, that reaction of pale green [$U(NN_3)(OPh)$], **6**, with [$Li(OBu^t)$] gave a turquoise solution that yielded the mixed alkoxide *ate* complex [$U(NN_3)(OBu^t)(OPh)Li(THF)$], **9**, on crystallization from pentane (59%). Mass spectra of **9** gave peaks corresponding to the species [$U(NN_3)(OPh)$]$^+$ and [$U(NN_3)(OBu^t)$]$^+$ arising from elimination of [$Li(OBu^t)$] and [Li(OPh)]. Reaction of the *tert*-butoxido derivative **3** with [Li(OPh)] and [$Li(OBu^t)$] gave **9** and [$U(NN_3)(OBu^t)_2Li(THF)$], **10**, respectively.

Complex salts with incorporated alkali metal ions are quite common in lanthanide and actinide chemistry. For example, Clark and Watkin have structurally characterized [$NaTh_2(OBu^t)_9$], in which the sodium atom is coordinated solely by triply- and doubly-bridging alkoxide ligands to the Th_2 core.[19] Sattelberger and co-workers have reported the U(III) arylamide [$U(NH\text{-}2,6\text{-}Pr^i_2C_6H_3)_5\{K(THF)_2\}_2$], in which two potassium ions are coordinated by arene rings as well as THF ligands.[20] Stewart

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(16) Knösel, F.; Roesky, H. W.; Edelmann, F. T. *Inorg. Chim. Acta* **1987**, *139*, 187.

(17) (a) Cotton, F. A.; Marler, D. O.; Schwotzer, W. *Inorg. Chim. Acta* **1984**, *85*, L31. (b) Cotton, F. A.; Marler, D. O.; Schwotzer, W. *Inorg. Chem.* **1984**, *23*, 4211.

(18) ^1H NMR spectra of complexes **3**−**7** at all accessible temperatures were consistent with 3-fold symmetry in the molecules, signals being observed over the usual range for U(IV) species.

(19) Clark, D. L.; Watkin, J. G. *Inorg. Chem.* **1993**, *32*, 1766.

(20) Nelson, J. E.; Clark, D. L.; Burns, C. J.; Sattelberger, A. P. *Inorg. Chem.* **1992**, *31*, 1973.

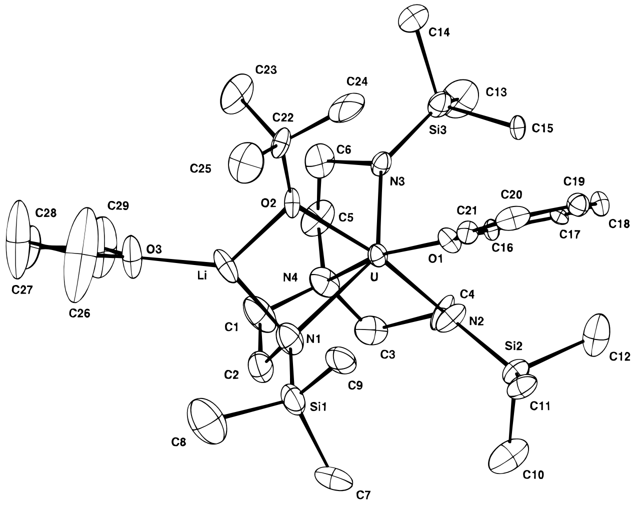

Figure 2. Thermal ellipsoid plot of the molecular structure of **9**. Hydrogen atoms are omitted.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **9**

U−O(1)	2.188(8)	Li−O(2)	1.86(3)
U−N(2)	2.274(12)	Li−O(3)	1.92(3)
U−N(3)	2.278(11)	Li−N(1)	2.01(4)
U−O(2)	2.294(10)	Si(1)−N(1)	1.740(14)
U−N(1)	2.408(12)	Si(2)−N(2)	1.724(12)
U−N(4)	2.680(12)	Si(3)−N(3)	1.675(11)
O(1)−U−N(2)	93.4(5)	O(2)−U−N(4)	104.0(4)
O(1)−U−N(3)	109.0(4)	N(1)−U−N(4)	68.2(4)
N(2)−U−N(3)	94.7(4)	O(2)−Li−O(3)	132.0(20)
O(1)−U−O(2)	93.1(4)	O(2)−Li−N(1)	95.4(14)
N(2)−U−O(2)	171.6(4)	O(3)−Li−N(1)	128.2(16)
N(3)−U−O(2)	88.2(4)	C(16)−O(1)−U	178.0(12)
O(1)−U−N(1)	121.6(4)	C(22)−O(2)−Li	123.5(13)
N(2)−U−N(1)	97.0(5)	C(22)−O(2)−U	139.5(8)
N(3)−U−N(1)	127.0(4)	Li−O(2)−U	97.1(11)
O(2)−U−N(1)	75.0(4)	C(2)−N(1)−Li	106.5(13)
O(1)−U−N(4)	162.4(5)	C(2)−N(1)−U	118.9(10)
N(2)−U−N(4)	70.0(4)	Li−N(1)−U	89.3(9)
N(3)−U−N(4)	68.0(4)	Si(1)−N(1)−Li	106.5(11)

and Andersen showed that addition of lithium methyl to $[\mathrm{U(OCHBu^t_2)_4}]$ gives $[\mathrm{LiU(OCHBu^t_2)_4Me}]$.[21]

Sublimation of pure **8** at 140 °C and 10^{-6} mbar gave **6** and involatile [Li(OPh)]. Similarly, **10** gave **3** at 60 °C. Sublimation of the pure mixed-alkoxide *ate* complex **9** at 60 °C/10^{-6} mbar gave pure *tert*-butoxido derivative **3** (Scheme 2). Surprisingly, none of the phenoxido derivative **6** could be detected even when the sublimation was performed at temperatures well above that at which pure **6** distills (140 °C). In the hope of explaining the high degree of selectivity for elimination of [Li(OPh)] from **9**, we decided to investigate its structure in the solid state.

An X-ray analysis of **9** yielded the molecular structure shown in Figure 2. Selected bond lengths and angles are given in Table 3. The orientation of the (triamidoamine)uranium fragment in this 6-coordinate species is only slightly distorted from trigonal monopyramidal, unlike that in pseudooctahedral $[\mathrm{U(NN_3)(\eta^3\text{-}BH_4)(THF)}]$,[5] and the approximate overall structure is that of a capped trigonal bipyramid with O(2) as the capping atom. A lithium atom is incorporated into the ligand sphere by coordination with the *tert*-butoxido ligand at O(2) and the amido nitrogen N(1); this leads to reduced N(pπ)−U overlap and a lengthening of the U−N(1) bond to 2.408(12) Å compared to 2.274(12) and 2.278(12) Å for U−N(2) and U−N(3), respectively. The geometry about N(1) is distorted from tetrahedral as a consequence of the atom O(2) bridging Li and U; the angle Li−N(1)−U is 89.3(9)°. One THF ligand makes up the approximate trigonal planar coordination at Li.

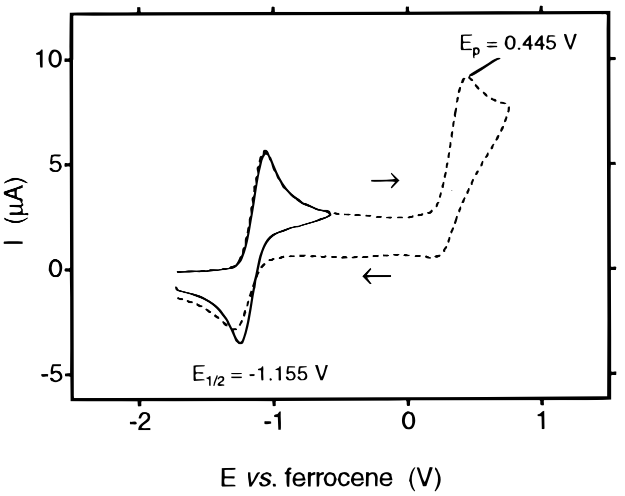

Figure 3. Cyclic voltammogram of **8** in THF/0.1 M $[\mathrm{Bu_4N}][\mathrm{PF_6}]$.

In solution or in the melt, it can be expected that the lithium ion in **9** will exchange between several sites on the molecule and that there will be an equilibrium concentration of material where it is bonded to the phenoxido oxygen. The exclusive elimination of [Li(OPh)] rather than $[\mathrm{Li(OBu^t)}]$ on heating of **9** *in vacuo* is explained by the relative insolubility of the former salt and by the fact that **3** is considerably more volatile than **6**.

The process **6** → **9** → **3** (Scheme 2) is a good example of an associative substitution reaction with an isolable intermediate of higher coordination number. We expect that the inherent flexibility of the triamidoamine fragment here will allow most nucleophilic substitution reactions of this system to proceed *via* such a pathway.

Electrochemical Studies: Synthesis of Pentavalent Alkoxides. Gilman demonstrated that hexavalent $[\mathrm{U(OEt)_6}]$ could be synthesized from pentavalent $\mathrm{Na[U(OEt)_6]}$ by oxidation with dibenzoyl peroxide.[22] We were interested as to whether the presence of a formal negative charge on the U atoms in **8**−**10** would facilitate their oxidation to 6-coordinate pentavalent complexes.

The cyclic voltammetric response of a THF solution of **8** saturated with tetrabutylammonium hexafluorophosphate is shown in Figure 3. The first wave at −1.155 V *versus* ferrocene is quasi-reversible ($\Delta E = 150$ mV at 200 mV s^{-1} with $i_{\mathrm{pa}}/i_{\mathrm{pc}} \approx 1.0$) but clean and reproducible (solid line), indicating the possibility of electrosynthesis of a U(V) species. Scanning to higher positive potential (dashed line) reveals a second irreversible wave ($E_{\mathrm{p}} = +0.445$ V) corresponding to oxidation to a U(VI) species and a subsequent homogeneous decomposition reaction. Unsurprisingly, no U(III)/U(IV) waves could be detected up to the cathodic dielectric breakdown. Complexes **9** and **10** gave similar cyclic voltammetric responses with the quasi-reversible waves at −0.97 and −1.04 V and irreversible waves at 0.745 and 0.86 V, respectively.

The potentials of the U(V)/(IV) couples of the *ate* complexes **8**−**10** indicate that these compounds could be oxidized by ferrocenium. Reaction of pure **8** with a stoichiometric amount of $[\mathrm{FeCp_2}][\mathrm{PF_6}]$ gave ferrocene and pentavalent $[\mathrm{U(NN_3)(OPh)_2}]$, **11**, as a red-brown solid in 77% yield. ^{1}H NMR

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spectra show that the two phenoxido groups are equivalent on this time scale and that the triamidoamine fragment has apparent 3-fold symmetry. The mixed alkoxides [U(NN$_3$)(OBu^t)(OPh)], **12**, and [U(NN$_3$)(OBu^t)$_2$], **13**, were prepared in a similar manner.

Clean electrochemical transformations of (non-uranyl) organoactinide species are rare.[23] The U(IV) alkoxide [U(O-2,6-Bu$^t_2$C$_6$H$_3$)$_4$] undergoes irreversible oxidation at a peak potential of *ca*. 0 V, while the U(III) homologue [U(O-2,6-Bu$^t_2$C$_6$H$_3$)$_3$] undergoes quasi-reversible oxidation at −1.22 V.[24] Oxidation of anionic U(IV) amides with [Tl(BPh$_4$)] affords the pentavalent derivatives.[25] We recently characterized the redox chemistry of a thorium diazabutadiene derivative.[6] That the first oxidation of **8** is not impaired by homogeneous decomposition reactions is probably due to a combination of the stability conferred by the chelate effect and the fact that the two alkoxido ligands required for steric saturation of the U(V) compound are already present.

Conclusion

By using the very bulky ligand {N(CH$_2$CH$_2$NSiMe$_2$Bu^t)$_3$}, we recently synthesized the first triamidoamine complex of the actinides with a trigonal geometry.[7] In this paper, we have shown that this structure type can also be achieved for the trimethylsilyl-substituted (NN$_3$) system by use of π-donating alkoxido auxiliary ligands, giving monomeric **3** and **5**−**7**. Nevertheless, given favorable steric properties, the [U(NN$_3$)(OR)] system may also form stable adducts with a second alkoxide ligand, giving complexes **8**−**10**. These complexes can be converted smoothly to the base-free alkoxide derivatives by sublimation. Finally, the U(V) bis(alkoxides) **11**−**13** can be prepared by stoichiometric oxidation of **8**−**10** in a process that has been characterized by cyclic voltammetry.

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Supporting Information Available: X-ray crystallographic files, in CIF format, are available on the Internet only. Access information is given on any current masthead page.

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