Inorg. Chem. **1999,** *38,* 3651−3656

Complexes of Triamidoamines with the Early Actinides. Synthetic Routes to Monomeric Compounds of Tetravalent Uranium and Thorium Containing Halide and Amide Ligands

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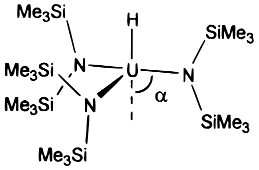
Received March 10, 1999

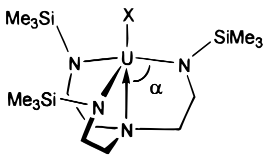
The reaction of the lithiated triamidoamine $[Li_3(NN'_3)(THF)_3]$ $[NN'_3 = N(CH_2CH_2NSiMe_2Bu^t)_3]$ with $AnCl_4$ (An = U, Th) followed by sublimation gives monomeric $[An(NN'_3)Cl]$. Reaction of these complexes with $SiMe_3X$ (X = Br, I) gives $[An(NN'_3)X]$. The amido derivatives $[An(NN'_3)(NEt_2)]$ are prepared from $H_3(NN'_3)$ and $[U(NEt_2)_4]$ and from $[Th(NN'_3)Cl]$ and $[Li(NEt_2)]$. In each case, the complexes $[U(NN'_3)X]$ (X = Cl, Br, I, NEt_2) are shown by X-ray crystallography to contain a triamidoamine ligand disposed with 3-fold symmetry about the metal center. The structures are distorted from trigonal bipyramidal by displacement of the uranium atoms out of the equatorial plane of the three amido nitrogen atoms by ca. 0.8 Å. The ligand backbone is distorted in such a manner as to cause the *tert*-butyldimethylsilyl groups to encircle the equatorial plane of the metal atom rather than surround the apical coordination site as is observed in the transition metal complexes of this type. Variation of the auxiliary ligand has little effect on the orientation, bond lengths, and angles within the (triamidoamine)uranium fragment. The *tert*-butydimethysilyl-substituted triamidoamine ligand is thus ideally suited for coordination to large metals since it stabilizes the formation of 3-fold symmetric structures while also allowing reactivity at the fifth coordination site.

Introduction

For the early actinides, sterically demanding ligands are generally required in order to generate low coordination number complexes. For example, monomeric amides of these elements are isolated most readily by use of very bulky ligands such as $-N(SiMe_3)_2$.[1] While one of the most commonly used of the triamidoamine[2] ligands $[N(CH_2CH_2NR)_3]^{3-}$ (R = $SiMe_3$) is closely related to the fragment $\{N(SiMe_3)_2\}_3$, these systems would be expected to have different steric demands because of the constraints of the chelate structure of the former. In the four-coordinate complex $[U\{N(SiMe_3)_2\}_3H]$, **I**, for example, the uranium sits 0.51 Å out of the plane defined by the three amido nitrogen atoms,[3] while in the few 3-fold symmetric triamidoamine complexes of the actinides $[U\{(Me_3SiNCH_2CH_2)_3N\}X]$, **II**, this distance is ca. 0.7−0.8 Å.[4] Also, the angle α in **I** is 77° while in **II** it lies in the range 67−71°. More commonly, such complexes of the early actinides tend to have unsymmetric structures unless strong π-donor coligands are used.[5] Hence, for the triamidoamines, substituent groups larger than trimethylsilyl are required to saturate sterically the actinide complexes.



I



II

We set out to tune the steric protection afforded by the substituents on the triamidoamine ligands such that the actinide complexes would have symmetric structures but also be reactive enough to be used in the exploration of the chemistry of the elements in this form. In this paper we will show that use of the *tert*-butyldimethylsilyl ligand $[N(CH_2CH_2NSiBu^tMe_2)_3]$ (henceforth NN'_3) achieves this aim and describe a convenient entry to this system via the preparation of monomeric, tetravalent actinide chlorides, bromides, iodides and amides. We have recently exploited this ligand in the formation of the first lanthanide triamidoamines[6] and a "trigonal monopyramidal" trivalent uranium compound which forms an unprecedented complex with dinitrogen.[7]

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10.1021/ic990563f CCC: $18.00

Experimental Section

All manipulations were carried out under an inert atmosphere of argon either using standard Schlenk techniques or in an MBraun drybox. Sublimation was performed by oven heating (±1 °C) of material under study contained in one end of a horizontal glass tube, dynamic vacuum in the system being maintained by a turbomolecular pumping system protected by a wide-bore liquid nitrogen cooled trap. NMR samples were made up in the drybox, and the sample tubes were sealed in vacuo or using Young's type concentric stopcocks. Solvents were predried over sodium wire and then distilled over potassium (tetrahydrofuran), sodium (toluene) or sodium-potassium alloy (diethyl ether, pentane) under an atmosphere of dinitrogen. Deuterated solvents were dried by refluxing over molten potassium in vacuo and then distilled trap-to-trap also in vacuo. NMR spectra were recorded at ca. 295 K on Bruker WM-360, AC-250, AC-400, or DMX-300 spectrometers and the spectra referenced internally using residual protio solvent resonances relative to tetramethylsilane ($\delta = 0$ ppm). Infrared spectra were obtained as Nujol mulls in an air-tight holder using a Perkin-Elmer FTIR spectrometer. Ultraviolet/visible/near-IR spectra were obtained as pentane solutions in an air-tight quartz cell of path length 0.1 cm using a Jasco V-540 spectrophotometer. EI mass spectra were obtained on a VG Autospec mass spectrometer by Dr. Abdul-Sada at the University of Sussex. Elemental analyses were performed by Canadian Microanalytical Services Ltd., Delta, BC, Canada, and Warwick Analytical Services. Cryoscopic solution molecular weight determinations were performed on ca. 200 mg samples in cyclohexane.[8] BCl_3 and $[Li(NEt_2)]$ were purchased from Aldrich Chemical Company Ltd. $ThCl_4$ was purchased from CERAC. Literature methods were used for the preparation of UCl_4,[9] $[Li_3(NN'_3)(THF)_3]$, **1**,[10,11] $[UI_3(THF)_4]$,[12] and $[\{U(NEt_2)_4\}_2]$.[13]

$[U(NN'_3)Cl]$, 2. Method A. Tetrahydrofuran (80 cm^3) was added at −80 °C to a mixture of $[Li_3(NN'_3)(THF)_3]$, **1** (8.00 g, 11.0 mmol), and UCl_4 (4.20 g, 11.0 mmol). The mixture was stirred for 1 h at ambient temperature to give a green solution. After evaporation of volatiles the residue was extracted with pentane (3 × 30 cm^3), filtered, and evaporated under reduced pressure (a green crystalline precipitate of virtually pure **2** is often formed at this stage). The residue was sublimated at 180 °C and 10^{-6} mbar to give a green crystalline solid (7.84 g, 94%), which may be further recrystallized from pentane at −30 °C.

Method B. Boron trichloride (1.3 cm^3, 1 M solution in hexanes, 1.1 equiv) was added to a solution of **8** (1 g, 1.3 mmol) in pentane (20 cm^3) at −50 °C. Immediate evaporation of volatiles and sublimation at 180 °C and 10^{-6} mbar gave a green crystalline solid (0.72 g, 76%).

Anal. Calcd for $C_{24}H_{57}N_4Si_3ClU$: C, 37.96; H, 7.56; N, 7.38. Found: C, 37.78; H, 7.48; N, 7.39. ^1H NMR (293 K, d_6-benzene): δ 7.7 (s, 6H, CH_2), 6.7 (s, 27H, Bu^t), 6.3 (s, 18H, Me_2Si), −23.8 (s, 6H, CH_2). MS (EI): *m/z* 759 (42%, M^+), 702 (100%, $M^+ - Bu^t$). IR (Nujol): 1260 (m), 1075 (m), 924 (m) 902 (w), 829 (m), 800 (m), 776 (w), 722 (m), 675 (w). UV/vis/near-IR: λ_{max} (nm) (ϵ, M^{-1} cm^{-1}) 452 (33), 468 (32), 488 (25), 528 (30), 582 (19), 620 (11), 690 (74), 706 (38), 826 (11), 880 (8), 954 (6), 1076 (37), 1108 (33), 1142 (37), 1192 (33), 1502 (16), 1648 (13), 1730 (16), 1774 (10), 1812 (8). Magnetic susceptibility (Evans method, 225−293 K): $\mu_{eff} = 3.19$ μ_B.

$[Th(NN'_3)Cl]$, 3. This was prepared similarly to **2** (method A) (94%).

Anal. Calcd for $C_{24}H_{57}N_4Si_3ClTh$: C, 38.26; H, 7.62; N, 7.44. Found: C, 38.15; H, 7.45; N, 7.40. ^1H NMR (293 K, d_6-benzene): δ 3.40 (t, 6H, CH_2), 2.23 (t, 6H, CH_2), 1.03 (s, 27H, Bu^t), 0.38 (s, 18H, Me_2Si). $^{13}C\{^1H\}$ NMR (293 K, d_6-benzene): δ 64.49 (s, CH_2), 47.03 (s, CH_2), 27.21 (s, Me_3C), 20.37 (s, $Me_3\mathit{C}$), −5.18 (s, Me_2Si). MS (EI): *m/z* 752 (12%, M^+), 717 (11%, $M^+ - Cl$), 695 (92%, $M^+ - Bu^t$). IR (Nujol): 1244 (m), 1192 (w), 1083 (m), 1023 (w), 982 (m), 931 (s), 835 (s), 768 (m), 722 (m).

$[U(NN'_3)Br]$, 4. Bromotrimethylsilane (0.21 g, 1.37 mmol) was added to a concentrated pentane (5 cm^3) solution of **2** (1.00 g, 1.32 mmol). Cooling the solution at −30 °C overnight afforded pale green needles (0.93 g, 88%).

Anal. Calcd for $C_{24}H_{57}N_4Si_3BrU$: C, 35.86; H, 7.15; N, 6.97. Found: C, 35.42; H, 7.24; N, 6.86. ^1H NMR (293 K, d_6-benzene): δ 8.8 (s, 18H, Me_2Si), 8.1 (s, 27H, Bu^t), 6.7 (s, 6H, CH_2), −29.3 (s, 6H, CH_2). MS (EI): *m/z* 804 (18%, M^+), 747 (45%, $M^+ - Bu^t$). IR (Nujol): 1334 (m), 1249 (s), 1169 (w), 1144 (m), 1061 (s), 1021 (s), 922 (s), 896 (s), 830 (s). UV: λ_{max} (nm) (ϵ, M^{-1} cm^{-1}) 454 (33), 468 (33), 498 (28), 526 (35), 584 (24), 688 (81), 624 (16), 648 (12), 830 (15), 878 (13), 900 (13), 954 (9), 1080 (44), 1140 (44), 1160 (44), 1190 (37), 1488 (20), 1624 (16), 1734 (19), 1776 (12), 1818 (10), 1986 (3). Magnetic susceptibility (Evans method, 225−293 K): $\mu_{eff} = 3.14$ μ_B.

$[Th(NN'_3)Br]$, 5. This was prepared similarly to **4** (90%).

Anal. Calcd for $C_{24}H_{57}N_4Si_3BrTh$: C, 36.13; H, 7.20; N, 7.02. Found: C, 36.25; H, 7.37; N, 7.19. ^1H NMR (293 K, d_6-benzene): δ 3.40 (t, 6H, CH_2), 2.34 (t, 6H, CH_2), 1.00 (s, 27H, Bu^tSi), 0.40 (s, 18H, Me_2Si). $^{13}C\{^1H\}$ NMR (293 K, d_6-benzene): δ 64.67 (s, CH_2), 47.12 (s, CH_2), 27.12 (s, Me_3C), 20.44 (s, $Me_3\mathit{C}$) −5.18 (s, Me_2Si). MS (EI): *m/z* 798 (14%, M^+), 741 (21%, $M^+ - Bu^t$). IR (Nujol): 1142 (w), 1077 (m), 1023 (w), 1005 (w), 925 (s), 896 (w), 827 (s), 800 (s), 774 (s), 722 (s).

$[U(NN'_3)I]$, 6. Method A. Iodotrimethylsilane (1.20 g, 6.00 mmol) was added to a concentrated solution of **2** (4.5 g, 5.93 mmol), in pentane (15 cm^3). The light green microcrystalline solid which precipitated over a few minutes was collected on a frit, washed with a little pentane, and dried in vacuo (4.80 g, 96%).

Method B. Toluene (20 cm^3) was added at −80 °C to a mixture of **1** (0.8 g, 1.1 mmol) and $[UI_3(THF)_4]$ (1 g, 1.1 mmol). The mixture was stirred for 1 h at ambient temperature to give a brown solution. After evaporation of volatiles the residue was extracted with hot pentane (3 × 10 cm^3) and filtered, affording a light green solution, which was concentrated and cooled to −30 °C to give a light green crystalline solid (0.3 g, 32%). Depending on the purity of the starting material, cooling the mixture to −30 °C may be required in order to obtain a high yield of **6**.

Anal. Calcd for $C_{24}H_{57}N_4Si_3IU$: C, 33.88; H, 6.75; N, 6.58. Found: C, 33.58; H, 6.60; N, 6.48. ^1H NMR (293 K, d_6-benzene): δ 11.42 (s, 18H, Me_2Si), 9.60 (s, 27H, Bu^t), 6.34 (s, 6H, CH_2), −32.87 (s, 6H, CH_2). MS (EI): *m/z* 850 (14%, M^+), 793 (30%, $M^+ - Bu^t$), 723 (7%, $M^+ - I$). IR (Nujol): 1251 (s), 1142 (m), 1060 (s), 1021 (m), 924 (s), 897 (m), 827 (m), 799 (s), 744 (s), 738 (s), 700 (s). UV λ_{max} (nm) (ϵ not available due to low solubility): 1744, 1160, 900, 586, 1626, 1140, 830, 524, 1466, 1082, 688, 1186, 954, 620. Magnetic susceptibility (Evans method, 225−293 K): $\mu_{eff} = 3.08$ μ_B.

$[Th(NN'_3)I]$, 7. This was prepared similarly to **6** (method A) (92%).

Anal. Calcd for $C_{24}H_{57}N_4Si_3ITh$: C, 34.12; H, 6.80; N, 6.63. Found: C, 34.73; H, 6.86; N, 6.57. ^1H NMR (293 K, d_6-benzene): δ 3.38 (t, 6H, CH_2), 2.29 (t, 6H, CH_2), 1.00 (s, 27H, Bu^t), 0.42 (s, 18H, Me_2Si). $^{13}C\{^1H\}$ NMR (293 K, d_6-benzene): δ 64.8 (s, CH_2), 47.24 (s, CH_2), 27.3 (s, Me_3C), 20.40 (s, $Me_3\mathit{C}$), −5.05 (s, Me_2Si). MS (EI): *m/z* 844 (5%, M^+), 829 (6%, $M^+ - Me$), 787 (100%, $M^+ - Bu^t$). IR (Nujol): 1336 (w), 1251 (m), 1141 (w), 1070 (s), 1022 (w), 925 (s), 896 (w), 826 (s), 773 (s), 738 (m), 704 (m).

$[U(NN'_3)(NEt_2)]$, 8. Method A. A solution of $H_3(NN'_3)$, **1** (6.35 g, 13.0 mmol), in pentane (40 cm^3) was added to a solution of $[\{U(NEt_2)_4\}_2]$ (6.84 g, 6.50 mmol) in pentane (20 cm^3) at −80 °C. The mixture was stirred for 12 h at ambient temperature. After evaporation of volatiles the residue was crystallized from minimum pentane at −30 °C to give light brown elongated cubes (2 crops, 8.1 g, 78%).

Method B. d_8-Toluene was added to a mixture of **2** (0.025 g, 0.03 mmol) and lithium diethylamide (0.003 g, 0.03 mmol) in an NMR tube to give a light brown solution. ^1H NMR indicated 100% conversion to **8**.

Anal. Calcd for $C_{28}H_{67}N_5Si_3U$: C, 42.24; H, 8.48; N, 8.80. Found: C, 42.05; H, 8.13; N, 8.56. ^1H NMR (293 K, d_6-benzene): δ 99.66 (s, 4H, $\mathit{C}H_2CH_3$), 62.79 (s, 6H, $CH_2\mathit{C}H_3$), 34.55 (s, 6H, $\mathit{C}H_2CH_2$), 3.74 (s, 6H, $CH_2\mathit{C}H_2$), −12.25 (s, 27H, Bu^t), −26.60 (s, 18H, Me_2Si). MS

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(EI): m/z 723 (100%, $M^+ - NEt_2$), 665 (18%, $M^+ - NEt_2 - Bu^t$). IR (Nujol): 1249 (s), 1155 (w), 1144 (w), 1058 (s), 1024 (m), 1006 (w), 928 (s), 891 (w), 826 (s), 804 (s), 787 (s), 771 (s), 740 (m), 715 (s), 657 (m). UV λ_{max} (nm) (ϵ M^{-1} cm^{-1}) 524 (32), 586 (16), 656 (25), 680 (19), 708 (34), 774 (12), 878 (11), 1088 (33), 1336 (16), 1498 (15), 1634 (12), 1794 (11). Magnetic susceptibility (Evans method, 225−293 K) $\mu_{eff} = 2.50\ \mu_B$.

[Th(NN′₃)(NEt₂)], 9. This was prepared similarly to **8** (method B) and was recrystallized from pentane (70%).

Anal. Calcd for $C_{28}H_{67}N_5Si_3Th$: C, 42.56; H, 8.55; N, 8.86. Found: C, 42.09; H, 8.40; N, 8.44. ^1H NMR (293 K, d_6-benzene): δ 3.4 (overlapping t, 6H, NCH_2CH_2 and q, 4H, NCH_2CH_3), 2.38 (t, 6H, CH_2), 1.20 (t, 6H, NCH_2CH_3), 1.04 (s, 27H, Bu^t), 0.27 (s, 18H, Me_2Si). ^{13}C-{^1H} NMR (293 K, d_6-benzene): δ 65.6 (s, CH_2), 46.2 (s, CH_2), 41.5 (s, CH_2CH_3), 28.1 (s, Me_3C), 21.0 (s, Me_3C), 15.1 (s, CH_2CH_3), −4.0 (s, Me_2Si). MS (EI): m/z 717 (100%, $M^+ - NEt_2$), 660 (45%, $M^+ - NEt_2 - Bu^t$). IR (Nujol): 1249 (s), 1155 (w), 1144 (w), 1058 (s), 1024 (m), 1006 (w), 928 (s), 891 (w), 826 (s), 804 (s), 787 (s), 771 (s), 740 (m), 715 (s), 657 (m).

Crystallography

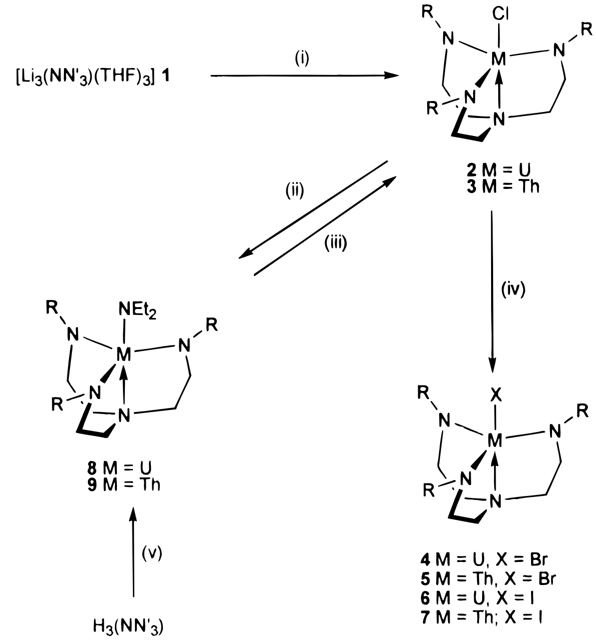
Crystals were coated with inert oil and transferred to the cold N_2 gas stream on the diffractometer (Siemens SMART three-circle with CCD area detector). Graphite-monochromated Mo K_α radiation $\lambda = 0.710\ 73$ Å was used. Absorption correction was performed by multiscan (SADAB). The structures were solved by direct methods using SHELXS[14] with additional light atoms found by Fourier methods. Hydrogen atoms were added at calculated positions and refined using a riding model with freely rotating methyl groups. Anisotropic displacement parameters were used for all non-H atoms; H atoms were given isotropic displacement parameters $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}(C)$ for methyl groups. The structures were refined using SHELXL 96.[15] The structures showed relatively large peaks in the final difference Fourier syntheses, but in all cases these were located close to the uranium atoms; they are attributed to series termination effects. For **2** the absolute structure of the individual crystal chosen was checked by refinement of the $\Delta F''$ multiplier. The absolute structure parameter x was 0.255(7).

Results and Discussion

Synthesis and Characterization of the Complexes [An(NN′₃)X] (An = U, Th; X = Cl, Br, I, NEt₂). We have reported the synthesis of the tris(trimethylsilyl)-substituted complexes [{An(NN₃)Cl}₂] (An = Th, U) in high yield from the reaction of [Li₃(NN₃)] with AnCl₄.[16] Using a similar approach, [Li₃(NN′₃)(THF)₃], **1**,[10] was treated with a stoichiometric amount of UCl₄ in THF. Sublimation of the product at 180 °C and 10^{-6} mbar gave pale green crystalline [U(NN′₃)Cl], **2**, in yields up to 93% on a scale of ca. 8 g (Scheme 1). This compound may be recrystallized from pentane at −20 °C.

Treatment of a solution of **2** in pentane with 1 equiv of bromotrimethylsilane followed by crystallization affords the tetravalent complex [U(NN′₃)Br], **4**. The iodo complex [U(NN′₃)I], **6**, was synthesised via reaction of **2** with iodotrimethylsilane. Conveniently, **6** is sparingly soluble in pentane and the pure solid precipitates from solution. Tetravalent **6** was also obtained in modest yield (32%) from the reaction between [UI₃(THF)₄][12] and **1**. A large amount of an intractable solid was also produced which presumably arises from disproportionation of the trivalent uranium starting material. A similar result was obtained on reaction of [UI₃(THF)₄] with Li[N(R)Ar].[17]

Scheme 1. Synthesis of the Complexes **1**−**9**[a]



[a] Key: (i) UCl₄/THF; (ii) Li(NEt₂); (iii) BCl₃/pentane; (iv) Me₃SiX (X = Br, I)/pentane; (v) [{U(NEt₂)₄}₂]/pentane.

Transamination is established as a versatile route to amido complexes of the early transition metals and actinides.[18] Edelstein and co-workers have characterized the products of the reaction between dimethylethylenediamine and [{U(NEt₂)₄}₂].[19] Clark et al. have reported the preparation of the mixed-amido complex [Th{N(SiMe₃)₂}₂(NMePh)₂].[20] Stewart and Andersen showed that addition of H₂NMES (MES = 2,4,6-C₆H₂Me₃) to trivalent [U{N(SiMe₃)₂}₃] gave [{U{N(SiMe₃)₂}₂}₂(μ-NHMES)₂].[21] It might be envisaged that, as a consequence of the chelate effect, this route would be particularly suitable for synthesis of triamidoamine complexes, and indeed the syntheses of zirconium[22] and molybdenum compounds have been achieved by this method. Accordingly, the reaction of H₃(NN′₃)[10] with [{U(NEt₂)₄}₂][13] in pentane gave [U(NN′₃)(NEt₂)], **8**, in high yield.

Treatment of a solution of **8** in d₆-benzene with a slight excess of BCl₃ or Me₃SiCl gave complete conversion to **2** as shown by ^1H NMR spectroscopy. Also reaction of **2** with 1 equiv of lithium diethylamide gave **8** in essentially quantitative yield.

The thorium complexes [Th(NN′₃)Cl], **3**, [Th(NN′₃)Br], **5**, [Th(NN′₃)I], **7**, and [Th(NN′₃)(NEt₂)], **9**, were prepared by the same methods as their uranium analogues.

^1H NMR spectra of the paramagnetic uranium compounds **2**, **4**, **6**, and **8** contain four broad peaks ($w_{1/2}$ ca. 10−50 Hz). On the basis of integration of the signals, two were assigned to the backbone methylene groups and one each to the *tert*-butyl

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Table 1. Experimental Data for the X-ray Diffraction Studies of **2**, **4**, **6**, and **8**

	2	**4**	**6**	**8**
empirical formula	$C_{24}H_{57}ClN_4Si_3U$	$C_{24}H_{57}BrN_4Si_3U$	$C_{24}H_{57}IN_4Si_3U$	$C_{28}H_{67}N_5Si_3U$
fw	759.49	803.95	850.94	796.17
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1$	$P2_1/c$	$P2_1/n$	$P2_1/n$
a/Å	22.7553(10)	29.923(6)	9.7632(10)	10.013(2)
b/Å	15.1678(10)	23.872(5)	22.5063(10)	23.364(3)
c/Å	22.7921(10)	20.837(4)	16.091(2)	16.599(3)
β/deg	116.69	107.81(3)	97.772(5)	99.2170(10)
cell vol/Å^3	7028.3(6)	14171(5)	3503.2(5)	3843.5(10)
Z	8	16	4	4
D_{calc}/Mg m^{-3}	1.436	1.507	1.613	1.376
$F(000)$	3040	6368	1664	1616
μ/mm^{-1}	4.815	5.828	5.635	4.339
temp/K	210(2)	180(2)	180(2)	200(2)
cryst size/mm	0.40 × 0.30 × 0.1	0.26 × 0.18 × 0.14	0.5 × 0.3 × 0.03	0.4 × 0.4 × 0.2
θ_{max}/deg	28.61	22.50	28.57	28.51
total reflns	42 973	56 111	21 068	22 995
indep reflns	24 510 [R(int) = 0.0771]	18 484 [R(int) = 0.1056]	8245 [R(int) = 0.0862]	8926 [R(int) = 0.0644]
significant reflns, $I > 2\sigma(I)$	21 578	9895	4809	5463
no. of params	1251	1248	314	350
T_{max}, T_{min}	1.00, 0.35	0.93, 0.71	0.928, 0.447	0.928, 0.484
GOF on F^2	1.242	1.125	0.813	0.909
(Δp) max, min (e Å^{-3}) (near U)	3.692, −3.620	3.699, −2.714	2.979, −2.940	1.928 , −1.710
R1, wR2 [$I > 2\sigma(I)$]	0.0611, 0.1574	0.0764, 0.1867	0.0496, 0.1029	0.0435, 0.0797

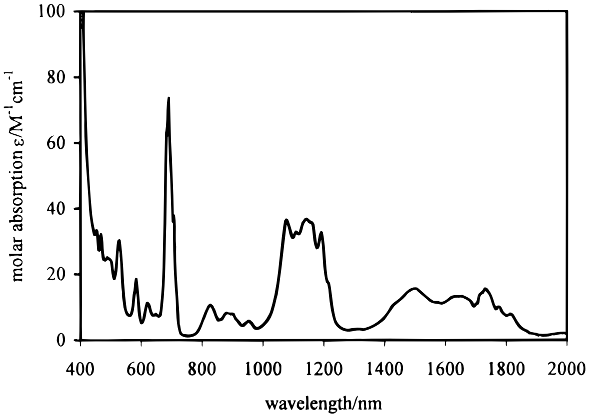

Figure 1. Absorption spectrum of [U(NN′$_3$)Cl], **2**, in pentane solution.

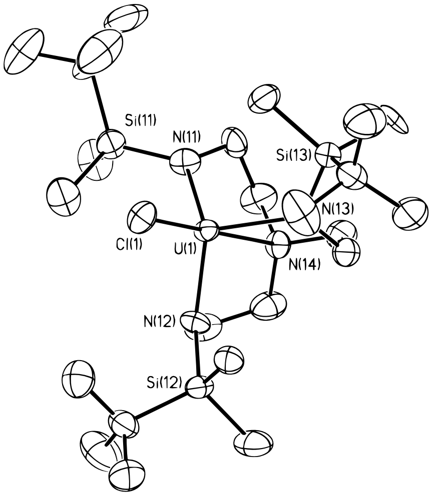

Figure 2. Thermal ellipsoid plot of the molecular structure of [U(NN′$_3$)Cl], **2**.

and dimethylsilyl groups. No variation in the number of signals was observed on cooling the samples to 180 K, indicating that, on the chemical shift time scale, these compounds have 3-fold symmetric structures in solution. The diamagnetic thorium complexes **3**, **5**, **7**, and **9** behave similarly.

Effective magnetic moments for the uranium complexes were determined in solution by the method of Evans between 225−293 K. Within this limited range, the compounds display apparent temperature independent paramagnetism. For the halides, μ_{eff} was found to be ca. 3.1−3.2 μ_B while that of the amide **8** was significantly lower at 2.50 μ_B. These are within the normal range for complexes of tetravalent uranium.

The UV/visible/near-IR spectra of pentane solutions of the halides **2**, **4**, **6**, and **8** contain several bands in the region 400−2000 nm with ϵ = <80 M^{-1} cm^{-1} presumably arising from f−f transitions. [23] The spectrum of the uranium chloride **2** (Figure 1), which is very similar to that of aqueous U(IV), is virtually superimposable with that of the bromide **4** in this region, and although comparison with that of the iodide **6** is less reliable because of the limited solubility of the latter in aliphatic hydrocarbons, its spectrum contains the same bands. The peak positions and molar absoption coefficients ϵ for the amide **8** differ somewhat from those for the halides, but the general features are similar.

Molecular Structures of [U(NN′)$_3$X] (X = Cl, Br, I, NEt$_2$)

Crystals suitable for X-ray crystallographic analysis (Table 1) of the uranium complexes **2**, **4**, **6**, and **8** were obtained by slow cooling of their solutions in pentane. A detailed description of the structure of the chloro complex **2** follows. Infrared spectra of the thorium complexes **3**, **5**, **7**, and **9** are virtually superimosable with those of the uranium analogues. Hence we propose that the analogous uranium and thorium compounds are isostructural.

The molecular structure of one of the four independent molecules in the asymmetric unit of **2** is shown in Figure 2. Selected bond lengths and angles appear in Table 2. The molecule possesses approximate C_{3v} symmetry with the nearly linear Cl(1)−U(1)−N(14) vector along the principal axis. The mean U−Cl bond distance of 2.662(11) Å is typical of tetravalent systems.[24] While the amido U−N$_{eq}$ distances of 2.20−2.24 Å are marginally shorter than the 2.23−2.28 Å observed in complexes [U(NN$_3$)X] of the tris(trimethylsilyl)-

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(23) Katz, J. J.; Morss, L. R.; Seaborg, G. T. *The Chemistry of the Actinide Elements*; Chapman Hall: New York, 1980.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **2**, **4**, **6**, and **8**[a]

	2 (X = Cl)	**4** (X = Br)	**6** (X = I)	**8** (X = NEt_2)
U−X	2.641(5)	2.823(2)	3.11	2.220(5)
U−N_{eq}	2.21(1)	2.22(1)	2.203(3)	2.271(3)
U−N_{ax}	2.67(2)	2.67(1)	2.685(6)	2.710(5)
N(4)−U(1)−X	178.6(5)	177.6(3)	177.53(12)	176.8(3)
displacement of U out of N_{eq} plane/Å	0.772	0.770	0.775	0.80
α/deg	67−71	68−71	69−70	69−70
dihedral angle N_{ax}−U−N_{eq}−Si/deg	136(5)	135(5)	130(3)	130(5)

[a] Data are averaged for all independent molecules where appropriate. Figures in parentheses indicate spread of data in last digit.

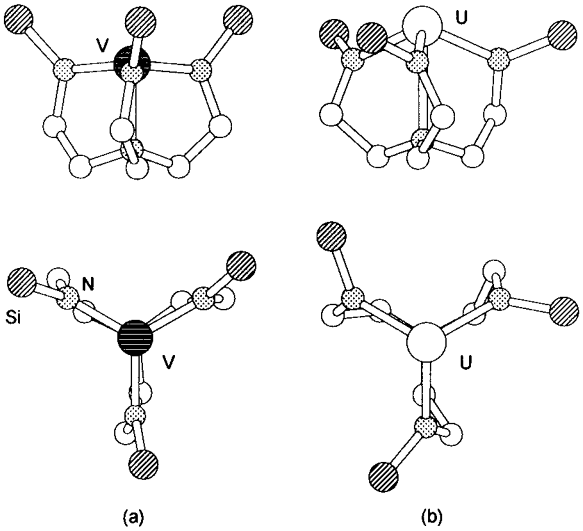

Figure 3. Projections of (a) [V(NN′$_3$)] and (b) [U(NN′$_3$)Cl], **2**, comparing (upper) displacement of the metal atoms out of the equatorial plane and (lower) the ligand conformation. Alkyl groups on the silicon atoms have been removed for clarity.

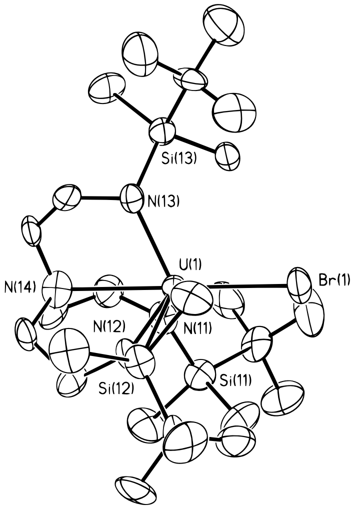

Figure 4. Thermal ellipsoid plot of the molecular structure of [U(NN′$_3$)Br] **4**.

triamidoamine ligand,[5] the mean amino U(1)−N(14) distance [2.656(19) Å] is longer than the values of 2.56−2.61 Å in these compounds. The substituents on the amido nitrogen atoms N(11)−N(13) have a planar arrangement, as usual. The inner coordination sphere of **2** is distorted from trigonal bipyramidal geometry by displacement of the UCl fragment by ca. 0.77 Å out of the plane defined by the amido nitrogen atoms; the angles α (vide supra) are 69−71°.

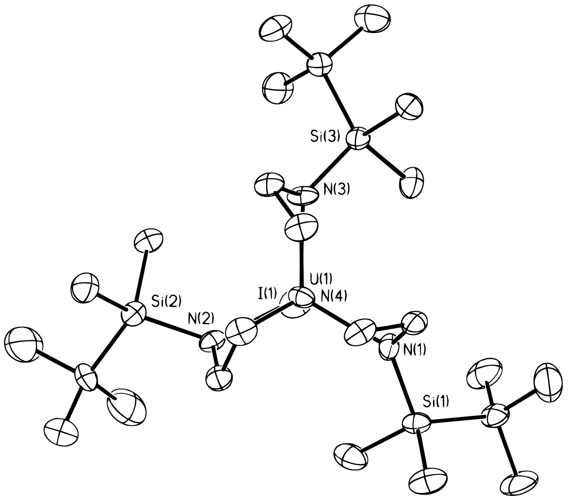

Figure 5. Thermal ellipsoid plot of the molecular structure of [U(NN′$_3$)I], **6**.

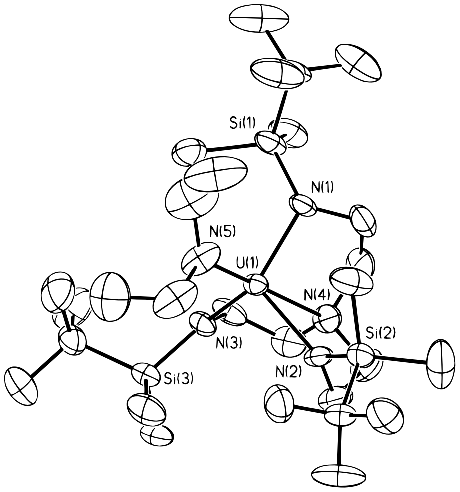

Figure 6. Thermal ellipsoid plot of the molecular structure of [U(NN′$_3$)NEt$_2$], **8**.

This coordination mode contrasts markedly with the distorted octahedral geometry of the trimethysilyl-substituted dimeric analogue [{U(NN$_3$)-μ-Cl}$_2$][16] but is similar to that observed for most transition metal triamidoamines. However, as a consequence of the larger radii of the actinides compared to the middle transition metals, the conformation of the ligand backbone is rather different. Figure 3 contains projections of the molecular structures of (a) trigonal monopyramidal [V(NN′$_3$)][11] and (b) [U(NN′$_3$)Cl], **2**; the Cl atom in **2** has been removed for clarity. The upper views compare the displacement of the metal atoms out of the equatorial plane and also show that, while the silicon atoms in [V(NN′$_3$)] encircle the apical coordination site, in **2** they protect the *equatorial plane* of the uranium atom. In order to maintain reasonable N_{ax}−U distances, the ligand in **2** must adopt a twisted conformation with dihedral angles N_{ax}−M−N_{eq}−Si in the range 136° ± 5° (vide infra). This angle is usually

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(24) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1.

(25) A notable exception to this is in [Ta(NN$_3$)Te], where the dihedral angles are in the range 138−156°. Presumably the steric demand of the Te atom forces the silyl groups downward, away from the axial site.

found to be 150−180° for transition metal complexes.[25] The lower view (b) also shows how the methylene carbons α to amido N are displaced from the approximate σ_v planes. This has the effect of directing the silyl groups to encircle the metal center.

The molecular structures of the bromide **4** (Figure 4), iodide **6** (Figure 5), and diethylamide **8** (Figure 6) are closely related to that of **2**. The bond lengths, angles, and conformation of the triamidoamine(metal) fragments are little affected by variation of the auxiliary ligand as appears from Table 2. The amido and amino bond distances $U-N_{ax}$ and $U-N_{eq}$ vary slightly across the series, the largest distances being observed for **8**, which contains the most sterically demanding auxiliary ligand. The distances from the U atom to the plane formed by the amido N atoms, the angle α (vide supra), and the range of dihedral angles $N_{ax}-M-N_{eq}-Si$ are essentially unaffected by variation of the ligand in the fifth coordination site.

Conclusion

Tetravalent actinide halides **2**−**7** and amides **8** and **9** are obtained from the pure trilithium salt **1** or $H_3(NN'_3)$ in high yields. These complexes are crystalline, soluble, and volatile and are excellent starting materials for exploration of the chemistry of actinide ions in a 3-fold symmetric environment. The molecular structures of **2**, **4**, **6**, and **8** show that, on coordination of the triamidoamine ligand to these large elements in a 3-fold symmetric fashion, a twist deformation occurs in the backbone. This leads to a reduction in the steric protection afforded to the remaining axial coordination site by the substituents on the amido nitrogen atoms, thus allowing reactivity at this position. For the ligand under study, however, the three *tert*-butyl groups are oriented such that they encircle the *equatorial plane* in *pseudo* trigonal pyramidal structures and thus stabilize this geometry. Thus the *tert*-butyldimethylsilyl-substituted triamidoamine seems to be ideally suited for synthesis and reactivity studies of these elements in a 3-fold symmetric environment. In our experience, the trimethylsilyl-substituted ligand is not sufficiently sterically demanding to produce monomeric species, while bulkier substituents such as Ph_2MeSi and $^iPr_3Si$ give rise to unreactive complexes.

Acknowledgment. P.S. thanks the EPSRC for a Project Studentship and SmithKline Beecham for a CASE award (to C.J.S.), Pfizer (UK) Ltd for a CASE award to I.J.M., Universitá degli Studi di Ferrara for support of R.B., and BNFL for a CASE award (to P.R.) and postdoctoral fellowship (to A.J.K.). We thank the EPSRC and Siemens Analytical Instruments for grants in support of the diffractometer.

Supporting Information Available: Four X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC990563F