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A Trigonal Bipyramidal Uranyl Amido Complex: Synthesis and Structural Characterization of $[Na(THF)_2][UO_2(N(SiMe_3)_2)_3]$

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The synthesis and structural characterization of a rare example of a uranyl complex possessing three equatorial ligands, $[M(THF)_2][UO_2(N(SiMe_3)_2)_3]$ (**3a**, M = Na; **3b**, M = K), are described. The sodium salt **3a** is prepared by protonolysis of $[Na(THF)_2]_2[UO_2(N(SiMe_3)_2)_4]$, whereas the potassium salt **3b** is obtained via a metathesis reaction of uranyl chloride $UO_2Cl_2(THF)_2$ (**4**) with 3 equiv of $K[N(SiMe_3)_2]$. A single-crystal X-ray diffraction study of **3a** revealed a trigonal-bipyramidal geometry about uranium, formed by two axial oxo and three equatorial amido ligands, with average U═O and U−N bond distances of 1.796(5) and 2.310(4) Å, respectively. One of the oxo ligands is also coordinated to the sodium counterion. ^1H NMR spectroscopic studies indicate that THF adds reversibly as a ligand to **3** to expand the trigonal bipyramidal geometry. The degree to which the coordination sphere in **3** is electronically satisfied with only three amido donors is suggested by (1) the reversible THF coordination, (2) a modest elongation in the bond distances for a five-coordinate U(VI) complex, and (3) the basicity of the oxo ligands as evidenced in the contact to Na. The vibrational spectra of the series of uranyl amido complexes $[UO_2(N(SiMe_3)_2)_n]^{2-n}$ ($n = 2-4$) are compared, to evaluate the effects on the axial U═O bonding as a function of increased electron density donated from the equatorial region. Raman spectroscopic measurements of the ν_1 symmetric O═U═O stretch show progressive axial bond weakening as the number of amido donors is increased. Crystal data for $[Na(THF)_2][UO_2(N(SiMe_3)_2)_3]$: orthorhombic space group $Pna2_1$, $a = 22.945(1)$ Å, $b = 15.2830(7)$ Å, $c = 12.6787(6)$ Å, $z = 4$, R1 = 0.0309, wR2 = 0.0524.

Introduction

The trans dioxo uranyl(VI) ion (UO_2^{2+}) is remarkably stable with respect to disruption of the U═O bond, which dominates the stereochemistry of its coordination compounds in both aqueous and nonaqueous solutions.[2] The linear O═U═O unit directs all other ligands to coordinate in an equatorial plane perpendicular to the O═U═O axis. In aqueous solution, uranyl coordination chemistry has been developed with a wide array of weak-field ligands that coordinate in the equatorial plane. In contrast, nonaqueous uranyl chemistry incorporating stronger donor ligands at equatorial sites has been less well developed.[3−7] Indeed, although amido ligands $(NR_2)^-$ are prevalent in lower valent uranium chemistry,[8−12] uranyl amido complexes are exceedingly rare.[13−15] This stems from the tendency of these strong σ- and π-donor ligands to reduce the U(VI) center, which severely limits the choice of substituents on the NR_2^- unit. Thus, to date, all known uranyl amido derivatives have employed the bis(trimethylsilyl)amido ligand $[N(SiMe_3)_2]^-$,[13−15] which has also proven to be versatile in stabilizing a variety of other uranium complexes within a wide range of oxidation states.[16−18] This silylamido ligand combines suitable steric and electronic properties, such that the high-valent U(VI) center is stabilized without the complication of reduction chemistry, and is sufficiently bulky to prevent oligomerization reactions.

Our interest in uranyl silylamido complexes is twofold. These species are stable with respect to reduction by the amido donors yet are considerably electron rich for a formally U(VI) center. This subtle electronic balance within a uranyl complex introduces interesting features in terms of structure, bonding, reactivity, and spectroscopic properties. In addition, various metal amido complexes have been demonstrated to be synthetically useful precursors in protonolysis reactions.[19,20] We are currently applying this methodology as an entry into nonaqueous

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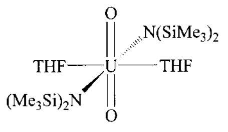
uranyl chemistry, with an aim toward probing the electronic effects of other ligands on the structure and bonding of the trans dioxo unit. Toward that end, we have previously reported the synthesis and structural characterization of two uranyl derivatives supported by $[N(SiMe_3)_2]^-$ ligands.[15] One is the neutral bis(amido) complex $UO_2(N(SiMe_3)_2)_2(THF)_2$ (**1**) first reported by Andersen[13] and determined by X-ray crystallographic data to be a monomeric species comprising mutually trans amido and THF ligands in the equatorial plane. The other is the anionic tetrakis(amido) derivative $[Na(THF)_2]_2[UO_2(N(SiMe_3)_2)_4]$ (**2**). An X-ray crystal structure of this complex has never been obtained; however, it is reasonable to conjecture that this species is monomeric as well, with the four equatorial amido ligands, as observed for the similarly bulky aryloxide complex $[Na(THF)_3]_2[UO_2(O\text{-}2,6\text{-}Me_2C_6H_3)_4]$.[15] Thus, **1** and **2** each possess four equatorial ligands, which is the minimum number of ligands commonly occupying the equatorial plane in uranyl complexes. Herein we report the synthesis and molecular structure of the third member within this series, the tris(amido) complex $[M(THF)_2][UO_2(N(SiMe_3)_2)_3]$ (**3a**, M = Na; **3b**, M = K). In contrast to the other two members, the electronic and steric balance for **3** is such that this complex represents a rare example of a structurally characterized uranyl complex with fewer than four equatorial ligands.[21]



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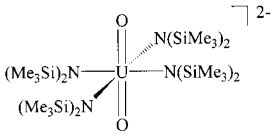

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Experimental Section

General Considerations. Unless otherwise stated, all manipulations were performed under an atmosphere of prepurified nitrogen in a Vacuum Atmospheres HE-553-2 glovebox equipped with a MO-40-2 purification system or in standard Schlenk-type glassware on a dual vacuum/nitrogen line. Tetrahydrofuran (THF), hexane, and toluene were dried by passage through a short column (5−6 cm) of activated alumina.[22] Benzene-d_6 and THF-d_8 were degassed and dried over KH prior to use. ^1H NMR spectra (referenced to either $C_6D_5\mathit{H}$ set at 7.15 ppm or $O(CD_2CD\mathit{H})_2$ set at 1.73 ppm for benzene and THF, respectively) were performed on a Varian XL-300 instrument. All chemical shifts are reported in parts per million, and all coupling constants are reported in hertz. Infrared spectra were obtained in Nujol mulls between KBr plates on a Bio-Rad Digilab FTS 40 spectrophotometer. Raman spectra were obtained by excitation from an Ar^+-pumped Ti sapphire laser (Spectra Physics, model 2025) operating at 754.5 nm. The power output from the laser (<40 mW) was minimized to inhibit sample degradation. The scattered light was analyzed on a SPEX model triple monochromator equipped with an 1800 groove/mm grating and a Photometrix CCD detector. $[UO_2Cl_2(THF_2)]_2$ (**4**),[23] **1**,[15] and **2**[15] were prepared according to published procedures. $NaN(SiMe_3)_2$ and $KN(SiMe_3)_2$ were obtained from Aldrich and recrystallized before use, and pentamethylcyclopentadiene (Aldrich) was used as received.

$[Na(THF)_2][UO_2(N(SiMe_3)_2)_3]$ (3a). Method a. A solution of pentamethylcyclopentadiene (C_5Me_5H; 102 mg, 0.74 mmol) in 15 mL of toluene was added dropwise with stirring to a solution of **2** (934 mg, 0.75 mmol) dissolved in 50 mL of toluene at 23 °C. The reaction mixture was left to stir for 24 h, during which the initial reddish-orange solution gradually darkened. The volatiles were then removed under vacuum, and the residue was extracted with THF and filtered through Celite. Orange-red crystals of **3a** were obtained from a cold (−40 °C) concentrated THF solution and washed with hexane. Yield: 0.58 g (85%). ^1H NMR (23 °C, C_6D_6): δ 0.62 (s, 54H, $Si(C\mathit{H}_3)_3$), 1.21 (m, 8H, $OCH_2C\mathit{H}_2$), 3.19 (m, 8H, $OC\mathit{H}_2CH_2$). IR: $\nu(U{=}O)$ 928 cm^{-1}. Raman: $\nu(U{=}O)$ 805 cm^{-1}. Anal. Calcd for $C_{26}H_{70}N_3NaO_4Si_6U$: C, 34.00; H, 7.68; N, 4.58. Found: C, 33.67; H, 7.51; N, 4.24. **Method b.** Toluene (40 mL) was added to a solid mixture of **2** (376 mg, 0.30 mmol) and $B(C_6F_5)_3$ (160 mg, 0.31 mmol) at 23 °C. The reaction mixture was left to stir at this temperature for 12 h, during which the initial reddish-orange solution gradually darkened. The solvent was then reduced to 10 mL, and orange-red crystals of **3a** were obtained at (−40 °C). Yield: 0.23 g (83%).

$[K(THF)_2][UO_2(N(SiMe_3)_2)_3]$ (3b). A solution of $KN(SiMe_3)_2$ (1.15 g, 5.77 mmol) in 20 mL of THF was added with stirring to a solution of **4** (0.92 g, 1.89 mmol) dissolved in 100 mL of THF at 23 °C. The initial bright yellow color of the uranyl solution immediately turned reddish-orange upon addition. The mixture was stirred at 23 °C for 2 days, after which the volume was reduced to 50 mL and filtered through Celite. The volume was subsequently reduced to 10 mL, and 2 mL of toluene was added. Dark red crystals of **3b** were obtained from this solution at −40 °C. Yield (approximate): 1.4 g (78%). ^1H NMR (23 °C, C_6D_6): δ 0.83 (s, 54H, $Si(C\mathit{H}_3)_3$), 1.22 (m, 8H, $OCH_2C\mathit{H}_2$), 2.56 (m, 8H, $OC\mathit{H}_2CH_2$). IR: $\nu(U{=}O)$ 926 cm^{-1}. Raman: $\nu(U{=}O)$ 802 cm^{-1}.

X-ray Crystallographic Analysis of 3a. An orange needle was mounted from a matrix of mineral oil onto a glass fiber. The crystal was immediately placed on a Bruker P4/CCD/PC diffractometer and cooled to 203 K using a Bruker LT-2 temperature device. The data were collected using a sealed, graphite-monochromatized Mo Kα X-ray source. A hemisphere of data was collected using a combination of ω and ø scans, with 30 s frame exposures and 0.3° frame widths. Data collection, initial indexing, and cell refinement were handled using SMART software.[24] Frame integration and final cell parameter calculation were carried out using SAINT software.[25] The final cell parameters were determined using a least-squares fit to 4402 reflections. The data were corrected for absorption using the SADABS program.[26] Decay of the reflection intensity was not observed.

The structure was initially solved in orthorhombic space group *Pnma* (No. 62) using direct methods and difference Fourier techniques. The initial solution revealed the uranium, silicon, sodium, and the majority of all of the non-hydrogen atoms positions. The remaining atomic positions were determined from subsequent Fourier synthesis. Refinement in space group *Pnma* was problematic, with anisotropic thermal ellipsoids, anomalous bond distances and angles, an R1 value of 0.08, and a failure to converge. At this juncture, the space group was changed to $Pna2_1$ (No. 33), and the refinement proceeded smoothly. Hydrogen atom positions were fixed (C−H = 0.96 Å for methyl and 0.97 Å for methylene). The hydrogen atoms were refined using the riding model, with isotropic temperature factors fixed to 1.2 (methylene) or 1.5 (methyl) times the equivalent isotropic U of the carbon atom to which they were attached. The final refinement included anisotropic temperature factors on all non-hydrogen atoms. Structure solution and graphics were performed using SHELXTL PC.[27] SHELX-93 was used for structure refinement and the creation of publication tables.[28] Additional details of data collection and structure refinement are listed in Table 1.

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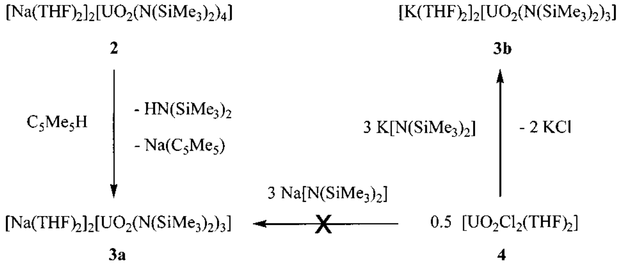
Table 1. Crystallographic Data for **3a**

formula	$C_{26}H_{70}N_3NaO_4Si_6U$	D_{calc}, g cm^3	1.372
fw	918.41	μ, mm^{-1}	3.851
cryst syst	orthorhombic	λ(Mo Kα), Å	0.710 73
space group	*Pna*2$_1$ (# 33)	temp, °C	−71
cell dimens		reflections collected	20 628
a, Å	22.945(1)	independent reflections	7514
b, Å	15.2830(7)	R1^a	0.0309
c, Å	12.6787(6)	wR2^b	0.0524
V, Å^3	4446.0(4)	gof	0.939
Z	4		

^{a} $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (0.014P)^2]$.

Scheme 1



Results and Discussion

Synthesis and Physicochemical Properties of [M(THF)$_2$][UO$_2$(N(SiMe$_3$)$_2$)$_3$] (3; M = Na, K). In an attempt to introduce a C_5Me_5 ligand to a uranyl species by a route that obviates the complications of reduction chemistry previously encountered with alkali-metal reagents, 1 equiv of pentamethylcyclopentadiene (C_5Me_5H) was added to the uranyl amido complex **2**. This reaction led to the successful protonation of one of the silylamido ligands of **2** and the subsequent elimination of HN(SiMe$_3$)$_2$ (Scheme 1), but instead of the anticipated nucleophilic attack of the resulting $C_5Me_5^-$ anion at uranium, the products obtained were NaC$_5$Me$_5$ and a new uranyl amido complex **3a**.

The products could be easily separated by cooling a THF solution of the reaction mixture to −40 °C, from which bright red crystals of air-sensitive **3a** were isolated. The sodium salt of tris(amido) **3a** could also be generated from **2** in reactions with other proton sources such as [NH$_4$][BPh$_4$], although the yields from these reactions were found to be lower. The generality of this reaction can be extended to Lewis acids such as B(C$_6$F$_5$)$_3$, which also abstracts an amido ligand from **2** to produce **3** in high yield.

Given the amido-abstracting reactions of tetrakis(amido) **2** to produce tris(amido) **3a**, we considered whether this complex could be generated more directly by a metathesis reaction of the uranyl chloro complex [UO$_2$Cl$_2$(THF$_2$)]$_2$ (**4**). However, the reaction of 3 equiv of NaN(SiMe$_3$)$_2$ with **4** led to roughly equal proportions of bis(amido) **1** and tetrakis(amido) **2**, with only trace amounts of **3a** discernible. Results were more satisfying upon switching to the potassium reagent KN(SiMe$_3$)$_2$, which permitted the formation of the potassium amido analogue **3b** in good yield as bright red crystals (Scheme 1). The low solubility of **3b** in THF, however, has thus far hampered an effective separation of this species from KCl generated from the reaction mixture.

In considering the different results obtained depending upon the choice of alkali reagent, it appears that the greater solubility of **3a** induced by the smaller Na cation renders it more susceptible to react further with NaN(SiMe$_3$)$_2$ to produce **2**. Conversely, the lower solubility of the K derivative **3b** effectively removes this species from further reactivity in solution.

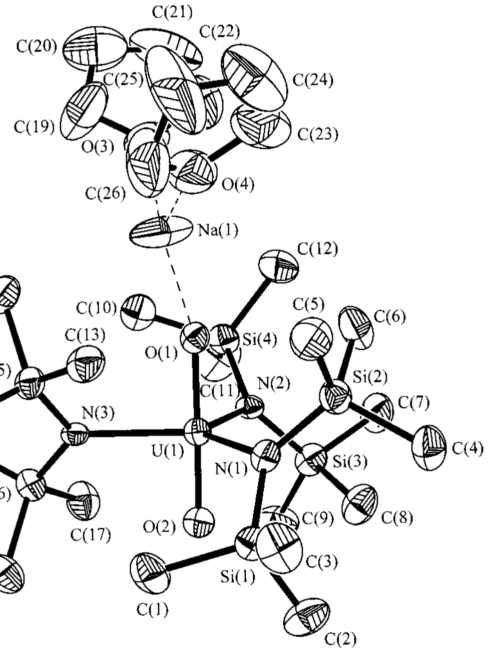


Figure 1. Thermal ellipsoid drawing of the repeat unit of [Na(THF)$_2$][UO$_2$(N(SiMe$_3$)$_2$)$_3$] illustrating the trigonal-bipyramidal coordination geometry about the uranium metal center and showing the atom-labeling scheme used in the tables.

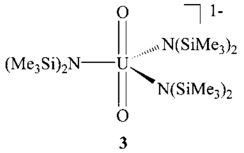
Table 2. Selected Bond Lengths [Å] and Bond Angles [deg] for **3a**

U(1)−O(2)	1.781(5)	O(2)−U(1)−O(1)	179.31(18)
U(1)−O(1)	1.810(5)	O(2)−U(1)−N(1)	89.62(18)
U(1)−N(1)	2.305(4)	O(1)−U(1)−N(1)	90.61(18)
U(1)−N(2)	2.306(4)	O(2)−U(1)−N(2)	90.07(17)
U(1)−N(3)	2.318(4)	O(1)−U(1)−N(2)	90.37(16)
U(1)−Si(1)	3.4638(18)	O(2)−U(1)−N(3)	90.79(18)
		O(1)−U(1)−N(3)	88.53(17)
Na(1)−O(1)	2.201(6)	N(1)−U(1)−N(2)	120.77(15)
Na(1)−O(4)	2.222(7)	N(1)−U(1)−N(3)	118.01(14)
Na(1)−O(3)	2.240(7)	N(2)−U(1)−N(3)	121.22(14)
N(1)−Si(2)	1.715(5)	O(1)−Na(1)−O(4)	128.4(3)
N(1)−Si(1)	1.740(5)	O(1)−Na(1)−O(3)	123.1(3)
Si(1)−C(2)	1.862(7)	O(4)−Na(1)−O(3)	100.8(3)
Si(1)−C(3)	1.887(6)	Si(2)−N(1)−Si(1)	120.7(3)
Si(1)−C(1)	1.887(7)	Si(2)−N(1)−U(1)	121.9(2)
		U(1)−O(1)−Na(1)	161.7(2)

Solid-State Molecular Structure of 3a. Single crystals of **3a** suitable for X-ray diffraction were obtained by the slow cooling of a THF solution. The data collection and crystallographic parameters are summarized in Table 1, and selected bond lengths and bond angles are given in Table 2. A thermal ellipsoid drawing of the repeat unit containing the atom-numbering scheme used in the tables is shown in Figure 1. The local coordination geometry about the UO$_2$[N(SiMe$_3$)$_2$]$_3^-$ ion is that of a relatively undistorted trigonal bipyramid, in which the trans oxo ligands O(1) and O(2) occupy axial coordination sites, whereas the three amido nitrogen atoms N(1), N(2), and N(3) occupy equatorial positions. There is an additional interaction of one of the oxo ligands to the THF-solvated Na cation. The trans dioxo unit of the uranyl group is nearly linear as exhibited by the O(1)−U−O(2) angle of 179.3(2)°. The axial−equatorial O−U−N bond angles span a relatively narrow range of 88.5−90.8(2)°, which together with the span of equatorial N−U−N angles between 118.0(2) and 121.2(2)° are consistent with trigonal-bipyramidal coordination geometry. The three amido N atoms are all trigonal planar, with a O−U−N−Si dihedral angle of approximately 38°, so that the amido ligands are oriented in a propeller-like arrangement, giving the anion an overall idealized C_3 symmetry. Whether this orientation of the silylamido ligands emanates from an electronic preference or is simply a function of crystal packing is uncertain.

The trigonal-pyramidal geometry about the sodium cation generated by the oxo interaction and two solvating THF ligands is rather unusual for sodium, which usually coordinates four or more ligands. Close inspection of the solid-state structure reveals two methyl groups from one of the silylamido ligands [C(13) and C(14)] oriented in relatively close proximity to the sodium ion. The Na(1)−C(13) and Na(1)−C(14) distances are 3.22(1) and 3.23(1) Å, respectively, which are rather long compared to the estimated van der Waals Na−C(methyl) contact of 3.16 Å.[29] The sodium coordination is, therefore, best described as a three-coordinate trigonal pyramid.

The U−O(1) bond distance of 1.810(5) Å is slightly longer than the U−O(2) distance of 1.781(5) Å because of the additional long-range contact to Na. In comparison, the normal range of U═O bond distances observed for the majority of uranyl complexes is 1.76−1.79 Å.[2] The U−N bond distances of 2.305(4)−2.318(4) Å in **3a** are comparable to or even a bit longer than the average U−N bond distances of 2.24 Å in U(IV)[11] and 2.30 Å in U(V)[17] complexes with analogous silylamido ligands. To the best of our knowledge, there are no structurally characterized uranyl(VI) amido complexes from which to draw comparisons. The quality of the crystallographic data obtained for **1** does not permit quantitative assessment of the bond lengths. However, a comparison can be made with the U(VI) imido species of the general formula $[UF(NR)(N(SiMe_3)_2)_3]$ (**5**),[18] which also displays an idealized trigonal-bipyramidal geometry with three $N(SiMe_3)_2^-$ ligands in the equatorial plane. The U−N(amido) bond lengths are considerably shorter in these neutral imido complexes at approximately 2.21−2.23 Å. The longer U−N bonds in **3a** can be attributed to a combination of the lower effective nuclear charge in this anionic complex, along with enhanced axial π bonding from the oxo ligands versus a fluoride donor in **5**.[30] Both of these factors contribute to increased electron density at the metal, thus weakening and lengthening the equatorial bonding. The relatively long U−N bonds in **3a**, therefore, suggest a fairly electronically satisfied coordination sphere, especially for a five-coordinate U(VI) complex. This argument could be extended to the U═O distances in **3a** as well, which are slightly elongated when compared to the average U═O bond length of 1.76−1.79 Å found in most six-coordinate uranyl complexes.[2] In general, the equatorial metal−ligand bond lengths in **3a** are expected to be shorter in comparison to those of the analogous uranyl complexes with higher equatorial coordination numbers, because fewer ligands will bind closer to the metal to maximize electron donation.[31]



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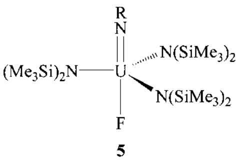

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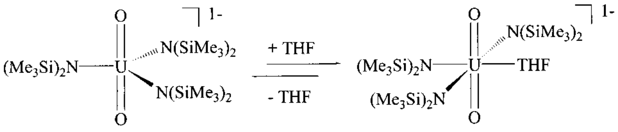
Solution Behavior of 3a. Tris(amido) **3a** is a rare example of a uranyl complex with fewer than four equatorial ligands.[21] The degree to which the coordination sphere in this complex is saturated is demonstrated by the absence of THF as a ligand in the solid-state molecular structure, despite being the crystallization solvent from which this complex is isolated. Nor is there evidence of an agostic interaction between the U metal center and the silylamido ligands in the solid state, where the U(1)−C(10) contact is nearest at 3.644(6) Å. However, **3** *can* incorporate an additional neutral donor ligand as indicated by ^1H NMR spectroscopy; the solution behavior described below is similar for both **3a** and **3b**. In benzene-d_6, one observes a single proton resonance in the ambient temperature ^1H NMR spectrum for the silylmethyl protons of the $N(SiMe_3)_2^-$ ligands. This is consistent with expectations for D_3 symmetry if one allows for fluxional coordination behavior with respect to the Na counterion. In THF-d_8 one observes a 2:1 ratio of silylmethyl peaks, indicative of a structure in solution that arises upon coordination of the donor solvent (eq 1) that destroys the C_3 axis of symmetry. The reversible nature of THF coordination in this species is indicated by the regeneration of trigonal-bipyramidal **3a** upon removal of the solvent. The significantly enhanced solubility of **3a** in THF relative to toluene and even diethyl ether is consistent with the inability of the latter solvents to solubilize the complex by coordinating to the metal center.



3 **3-THF** (1)

The solution studies suggest that sufficient electronic donation is provided by the three bulky silylamido ligands, thus rendering the addition of another donor optional. By comparison, the bis(amido) complex **2** requires *two* additional neutral donors (either THF[15] or $Ph_3P═O$[14]), and employing aryloxide ligands in $[UO_2(O\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_2(py)_3]$[15] necessitates further augmentation from *three* pyridine donors, despite the steric bulk of the anionic ligands. Evidently, a five-coordinate geometry is considerably more difficult to attain in neutral uranyl complexes, and electronic unsaturation seems to be as much of a factor as are steric considerations.

Metal−Ligand Bonding in Electron-Rich Uranyl Complexes. The strong axial U═O bonding in the vast majority of uranyl complexes is remarkably robust and remains relatively unperturbed by modification of the labile equatorial ligands.[32] However, one interesting aspect of anionic uranyl complexes incorporating basic alkoxide and amide donors in the equatorial plane is how the increased electron density supplied by these ligands is manifested in substantial weakening and lengthening of the U═O bonds.[33,34] Increased σ donation in the equatorial plane about the metal center generates increased electrostatic repulsion between the metal and the axial oxo groups, whereas strong π donation in the equatorial plane can effectively compete with the axial oxo ligands for the use of the same U 6d orbitals for π bonding. The latter argument has been proposed to account for the unprecedented lability of axial U═O bonds in the presence of π-donor OH^- ligands in $UO_2(OH)_4^{2-}$.[34]

The average U═O bond length of 1.795(5) Å in tris(amido) **3a** can be compared to the rather long U═O bond lengths of

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1.792(4), 1.789(4), 1.814(4), and 1.82(1) Å observed in $UO_2(O\text{-}t\text{-}Bu)_2(OPPh_3)_2$,[14] $UO_2(O\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_2(py)_3$,[15] $UO_2(O\text{-}2,6\text{-}Me_2C_6H_3)_4^{2-}$,[15] and $UO_2(OH)_4^{2-}$,[34] respectively. The latter compounds all contain π-donor ligands in the equatorial plane. The U═O bond lengthening is accompanied by an increase in Lewis basicity of the oxo groups as demonstrated by the O(1)−Na(1) interaction in **3a**, which at 2.201(6) Å is comparable to the average bond distance of 2.231(7) Å between the Na(1) and the O donors of the THF ligands. Increased basicity of the oxo ligands has also been observed in $[Na(THF)_3]_2[UO_2(O\text{-}2,6\text{-}Me_2C_6H_3)_4]$,[15] which shows a U═O···Na interaction, and through extensive U═O···H hydrogen bonding observed in $[Co(NH_3)_6]_2[UO_2(OH)_4]_3$.[34] Finally, we note that a more accurate representation of the U═O bond strength may be obtained from the ν_1 symmetric O═U═O stretch determined from Raman spectroscopy. The Raman spectra obtained from crystalline samples of bis(amido) **1**, tris(amido) **3a**, and tetrakis(amido) **2** reveal the ν_1 symmetric O═U═O stretch at 819, 805, and 801 cm^{-1}, respectively. The IR spectra reveal a similar trend with the ν_3 asymmetric O═U═O stretch at 935, 928, and 925 cm^{-1}, respectively. These data show a progressive weakening in the axial bonding with an increasing number of amido donors in the coordination sphere. For comparison, the U═O bond distance and ν_1 frequency of the aquo ion, $UO_2(OH_2)_5^{2+}$, are 1.76(1) Å[35] and 870 cm^{-1}.[36]

The trend of increasing metal basicity on passing from bis(amido) **1** to tetrakis(amido) **2** indicated by the Raman data is supported by the observation that **2** reacts with either C_5Me_5H or $B(C_6F_5)_3$ to produce tris(amido) **3**, whereas **1** remains unreactive in the presence of either substrate under the same conditions. However, from a steric point of view, the reaction of bulky substrates such as C_5Me_5H and $B(C_6F_5)_3$ with a silylamido ligand in a presumably crowded coordination sphere as found in **2** seems untenable at first. We have considered two possible mechanisms that may obviate these steric complications. In the first postulated mechanism, a combination of an electronically saturated and sterically crowded coordination environment in **2** may promote a degree of ligand dissociation, perhaps assisted by the sodium counterion. An equilibrium involving partial dissociation of a silylamido ligand may then expose this group to electrophilic attack by an acidic substrate (either a Brønsted or Lewis acid) to give **3**. However, the addition of excess $NaN(SiMe_3)_2$ to a solution of **2** shows no evidence in the ^1H NMR spectrum for an exchange process with coordinated silylamido ligands, which suggests that this mechanism (ligand dissociation) is not operative in **2**. Therefore, we currently favor a second more straightforward mechanism entailing initial electrophilic attack at an accessible uranyl oxo group, followed by a rearrangement in which the substrate is transferred to a silylamido leaving group.

Conclusion

Utilization of the steric and electronic properties of the amido donor $N(SiMe_3)_2^-$ has permitted the isolation and structural characterization of a rare example of a uranyl complex with three equatorial ligands. The five-coordinate tris(amido) complex **3a** can only be synthesized from protonolysis of tetrakis(amido) **2**, whereas alternatively the potassium derivative **3b** can only be obtained by salt metathesis from the uranyl chloride **4**. The solid-state structural data, solution behavior, and vibrational studies suggest that the trigonal-bipyramidal geometry in **3** is fairly electron-rich. However, the addition of an excess of THF does result in the reversible coordination of this neutral donor ligand.

Tris(amido) **3** is the third member of a series of silylamido uranyl complexes to be isolated. An examination of the Raman spectroscopic data reveals a trend of increasing electron density at the metal center as the number of silylamido ligands increases. This trend culminates with tetrakis(amido) **2**, which undergoes an abstraction reaction of a silylamido ligand by relatively bulky acidic substrates, perhaps via an initial electrophilic attack at a basic uranyl oxo site, to give tris(amido) **3**.

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Supporting Information Available: X-ray crystallographic file, in CIF format, for the structure determination of $[Na(THF)_2][UO_2(N(SiMe_3)_2)_3]$. This material is available free of charge via the Internet at http://pubs.acs.org.

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