

Articles

Reaction of the Uranyl(VI) Ion (UO_2^{2+}) with a Triamidoamine Ligand: Preparation and Structural Characterization of a Mixed-Valent Uranium(V/VI) Oxo–Imido Dimer

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The synthesis and structural characterization of a mixed-valent uranium(V/VI) oxo–imido complex are reported. Reaction of the uranyl chloride complex $[\text{K}(18\text{-crown-6})_2][\text{UO}_2\text{Cl}_4]$ (**1**) with the triamidoamine ligand $\text{Li}_3[\text{N}(\text{CH}_2\text{CH}_2\text{NSiBu}^t\text{Me}_2)_3]$ yields oxo–imido $[\text{K}(18\text{-crown-6})(\text{Et}_2\text{O})][\text{UO}(\mu_2\text{-NCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2\text{NSiBu}^t\text{Me}_2)_2)_2]$ (**2**) as the major isolated uranium product in moderate yield. The reaction that forms **2** involves activation of both the triamidoamine ligand and the uranyl dioxo unit of **1**. An X-ray crystal structure determination of **2** reveals a dimeric complex in which the coordination geometry at each uranium center is that of a capped trigonal bipyramid. The multidentate triamidoamine ligand coordinates to uranium through the capping amine and two of the three pendant amido ligands, while the third pendant amido donor has been activated to generate a bridging imido ligand by loss of the silyl substituent. One of the uranyl oxo groups is retained as a terminal ligand to complete the coordination sphere for each uranium center. The oxo and imido nitrogen may be regarded as the axial ligands of the trigonal bipyramid, while the two amido ligands and the other imido donor occupy equatorial coordination sites. The central amine of the tripodal set serves as the capping ligand. Distortion of the axial O–U–N angle from 180° emanates from the proximity of the capping amine and the bridging interaction to the other uranium center. The structure and bonding in **2** are assessed in the context of metal–ligand multiple bonding in high-valent actinide complexes. The possibility of valence averaging [5.5/5.5 vs 5.0/6.0] via delocalization or rapid intramolecular electron-transfer dynamics of the unpaired electron is also discussed in the context of crystallographic, spectroscopic (NMR, IR, Raman, and EPR), and electrochemical data. Crystal data for **2**: triclinic space group $P\bar{1}$, $a = 12.1144(6)$ Å, $b = 12.6084(6)$ Å, $c = 14.5072(7)$ Å, $\alpha = 101.374(1)^\circ$, $\beta = 103.757(1)^\circ$, $\gamma = 109.340(1)^\circ$, $z = 1$, $R1 = 0.0523$, $wR2 = 0.1359$.

Introduction

The role of f-orbitals in metal–ligand multiple bonding in high-valent uranium complexes is a topic of considerable interest in actinide chemistry.² This subject is currently being pursued in our laboratory within two classes of complexes. One class includes the aqueous and nonaqueous coordination chemistry of the trans dioxo uranyl(VI) ion (UO_2^{2+}),^{3–7} while the other entails the synthesis and reactivity of complexes of U(VI) stabilized by ancillary bis(cyclopentadienyl) ligand sets.^{8–10} For

all of these complexes, there are two ligands engaged in multiple bonding to the uranium center, involving either an oxo group or the isolobal imido ($=\text{NR}$) moiety. However, there is an important difference between the separate categories being studied. In all of the structurally characterized uranyl complexes, a trans dioxo $\text{O}=\text{U}=\text{O}$ unit is observed, both in solution and in the solid state. In contrast, the bent metallocene framework in complexes of the general formula $(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}(=\text{NR})(=\text{X})$ ($\text{X} = \text{O}, \text{NR}'$) enforces a cis geometry between the two multiply bonded ligands. Despite the ability to prepare a variety of cis oxo–imido complexes, a cis dioxo analogue of the uranyl species (i.e., $(\eta^5\text{-C}_5\text{Me}_5)_2\text{U}(=\text{O})_2$) has been unattainable thus far. Synthetic attempts in this regard have been hampered by reduction of the uranium(VI) center.⁸ Indeed, in sharp contrast to the ubiquitous nature of the trans uranyl ion, a cis dioxo complex of uranium remains elusive.

In an attempt to understand the origins of this difference, an alternate strategy to the synthesis of a uranium(VI) cis

(1) (a) LANL Mail Stop J514. (b) LANL Mail Stop J515. (c) LANL Mail Stop J755. (d) LANL Mail Stop E500.

(2) Katz, J. J.; Seaborg, G. T.; Morss, L. R. *The Chemistry of the Actinide Elements*; Chapman and Hall: London, 1986.

(3) Allen, P. G.; Bucher, J. J.; Clark, D. L.; Edelstein, N. M.; Ekberg, S. A.; Gohdes, J. W.; Hudson, E. A.; Kaltsoyannis, N.; Lukens, W. W.; Neu, M. P.; Palmer, P. D.; Reich, T.; Shuh, D. K.; Tait, C. D.; Zwick, B. D. *Inorg. Chem.* **1995**, *34*, 4797.

(4) Clark, D. L.; Conradson, S. D.; Donohoe, R. J.; Keogh, D. W.; Morris, D. E.; Palmer, P. D.; Rogers, R. D.; Tait, C. D. *Inorg. Chem.* **1999**, *38*, 1456.

(5) Wilkerson, M. P.; Burns, C. J.; Paine, R. T.; Scott, B. L. *Inorg. Chem.* **1999**, *38*, 4156.

(6) Wilkerson, M. P.; Burns, C. J.; Dewey, H. J.; Martin, J. M.; Morris, D. E.; Paine, R. T.; Scott, B. L. *Inorg. Chem.* **2000**, *39*, 5277.

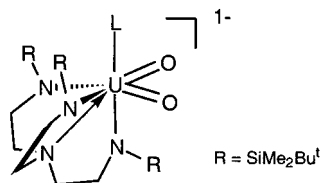
(7) Burns, C. J.; Clark, D. L.; Donohoe, R. J.; Duval, P. B.; Scott, B. L.; Tait, C. D. *Inorg. Chem.* **2000**, *39*, 5464.

(8) Arney, D. S. J.; Burns, C. J. *J. Am. Chem. Soc.* **1995**, *117*, 9448.

(9) Warner, B. P.; Scott, B. L.; Burns, C. J. *Angew. Chem., Int. Ed.* **1998**, *37*, 959.

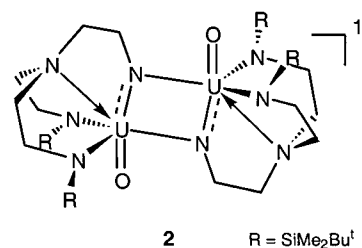
(10) Schnabel, R. C.; Scott, B. L.; Smith, W. H.; Burns, C. J. *J. Organomet. Chem.* **1999**, *591*, 14.

dioxo complex has been examined. Rather than attempting to introduce two oxo groups to a precursor metallocene complex in which the geometry is predisposed for cis coordination, it may be possible to react a uranyl complex with a suitable ligand set that directs the trans dioxo unit toward a cis geometry. As illustrated below, the triamidoamine ancillary ligand $[\text{N}(\text{CH}_2\text{CH}_2\text{NR})_3]^{3-}$ is ideal to test this hypothesis. Variations of this ligand set have been employed for a number of main group elements,¹¹ transition metals,^{12,13} lanthanides,¹⁴ and actinides.^{15–17} The triamidoamine ligand with the bulky silylamido substituent SiBu^tMe_2 has proven to be extremely versatile in the development of a rich uranium chemistry in Scott's group,^{18,19} including the isolation of the first actinide complex coordinated by dinitrogen.²⁰ For the current purpose, $[\text{N}(\text{CH}_2\text{CH}_2\text{NSiBu}^t\text{Me}_2)_3]^{3-}$ serves as a multidentate ligand that coordinates in a tripodal geometry designed to preclude a trans dioxo group of the uranyl ion and direct this unit instead toward a cis configuration. Additionally, strong donor ligands that coordinate in the equatorial plane have been demonstrated to weaken and labilize the axial $\text{O}=\text{U}=\text{O}$ bonding in uranyl complexes,^{4,21} and density functional theory calculations have even predicted a local energy minimum for the cis structure.²² Therefore, the incorporation of three strong donor amides as pendant donors in the triamidoamine ligand is anticipated to destabilize the trans dioxo unit of the uranyl, rendering a cis geometry more energetically favorable.



The reaction of $[\text{N}(\text{CH}_2\text{CH}_2\text{NSiBu}^t\text{Me}_2)_3]^{3-}$ with a uranyl chloride complex poses conflicting preferences between that of the ancillary ligand to chelate in a four-coordinate tripodal geometry, versus the overwhelming tendency of the uranyl dioxo unit to adopt a trans linear configuration. Indeed, this conflict is realized in the mutual activation of both the dioxo fragment and the triamidoamine ligand, and despite the nonreducing electronic nature of silyl-substituted amide ligands,⁷ one-electron reduction of the nominal U(VI/VI) unit also occurs in this reaction. An unusual mixed-valent uranium(V/VI) oxo–imido dimer (**2**) is generated as the major product. In this paper, we discuss the structure, bonding, and electronic factors associated with this complex in the context of metal–ligand multiple bonding in high-valent uranium chemistry.

- (11) Verkade, J. G. *Acc. Chem. Rev.* **1993**, 26, 483.
 (12) Cummins, C. C.; Lee, J.; Schrock, R. R.; Davis, W. M. *Angew. Chem., Int. Ed. Engl.* **1992**, 31, 1501.
 (13) Greco, G. E.; Popa, A. I.; Schrock, R. R. *Organometallics* **1998**, 17, 5591.
 (14) Roussel, R.; Alcock, N. W.; Scott, P. *Chem. Commun.* **1998**, 801.
 (15) Scott, P.; Hitchcock, P. B. *Polyhedron* **1994**, 13, 1651.
 (16) Scott, P.; Hitchcock, P. B. *J. Chem. Soc., Dalton Trans.* **1995**, 603.
 (17) Roussel, P.; Hitchcock, P. B.; Tinker, N. D.; Scott, P. *Inorg. Chem.* **1997**, 36, 5716.
 (18) Roussel, P.; Hitchcock, P. B.; Tinker, N.; Scott, P. *Chem. Commun.* **1996**, 2053.
 (19) Boaretto, R.; Roussel, P.; Alcock, N. W.; Kingsley, A. J.; Munslow, I. J.; Sanders, C. J.; Scott, P. *J. Organomet. Chem.* **1999**, 591, 174.
 (20) Roussel, P.; Scott, P. *J. Am. Chem. Soc.* **1998**, 120, 1070.
 (21) Burns, C. J.; Sattelberger, A. P. *Inorg. Chem.* **1988**, 27, 3692.
 (22) Schreckenbach, G.; Hay, P. J.; Martin, R. L. *Inorg. Chem.* **1998**, 37, 4442.



Experimental Section

General Information. 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 by using standard Schlenk-type glassware on a dual vacuum/nitrogen line. Tetrahydrofuran (THF), diethyl ether, hexanes, and toluene were dried by passage through a short column (5–6 cm) of activated alumina. Benzene-*d*₆ and THF-*d*₈ were degassed and dried over KH prior to use. ¹H NMR spectra (referenced to C₆D₅H set at 7.15 ppm) were performed on a Varian XL-300 Unity spectrometer. ¹³C NMR spectra (referenced to solvent peaks set at 128 ppm for C₆D₆) were run at 75.429 MHz on the XL-300 instrument. All chemical shifts are reported in ppm, and all coupling constants are reported in Hertz. EPR spectra were measured with an IBM (Bruker) series ER 200 X-band spectrometer equipped with a Hewlett-Packard 5350B microwave frequency counter and liquid nitrogen cryostat. The sample was measured at 100 K as a 1 mM toluene glass. Infrared spectra were obtained as Nujol mulls between KBr plates on a Bio-Rad Digilab FTS 40 spectrophotometer. FT Raman spectra were acquired on a Nicolet model 560 Magna-IR instrument equipped with a model 960 Raman attachment using the 1064 nm laser line from the Nd:VO₄ laser. Samples were run in sealed capillary tubes. It was necessary to run the samples as solids diluted with spectroscopy-grade KBr to minimize local heating and decomposition of the complex at the point of laser excitation. Cyclic voltammetric studies were conducted with a Perkin-Elmer Princeton Applied Research Corp. (PARC) model 263 potentiostat under computer control using M270 software. Samples were run in 0.1 M tetrabutylammonium hexafluorophosphate solution in tetrahydrofuran at a platinum working electrode with a silver wire quasi-reference electrode either in a PARC microcell in the glovebox or in a Schlenk cell. Measured potentials were calibrated using the ferrocene/ferrocenium couple ($E_{1/2} \approx 0.55$ V vs NHE), although there did appear to be some reaction between the ferrocene and **2** that leads to added uncertainty in the reported potentials for the redox processes of **2**. Elemental analyses were performed on a Perkin-Elmer 2400 CHN analyzer utilizing sealed aluminum capsules for delivery. Li₃[N(CH₂CH₂NSiBu^tMe₂)₃]²³ and [K(18-crown-6)]₂[UO₂Cl₄] (**1**)²⁴ were prepared according to published procedures.

[K(18-crown-6)(Et₂O)]₂[UO(μ₂-NCH₂CH₂N(CH₂CH₂NSiBu^tMe₂)₂)₂] (2**).** A solution of Li₃[N(CH₂CH₂NSiBu^tMe₂)₃] (500 mg, 0.68 mmol) in 20 mL of THF was added dropwise with stirring to a yellow slurry of **1** (750 mg, 0.68 mmol) in 20 mL of THF at 23 °C. The color of the reaction mixture immediately turned dull reddish-orange upon addition. The mixture was stirred for 12 h, the volatiles were removed under vacuum, and the residue was extracted with diethyl ether and filtered through Celite. Red crystals of **2** were obtained from a cold (–30 °C) concentrated diethyl ether solution and washed with cold hexanes. Yield 244 mg (44%). ¹H NMR (23 °C, C₆D₆): δ 3.6 (br s). IR/Raman: ν(U=O) 827 cm⁻¹. Anal. Calcd for C₅₂H₁₁₈KN₈O₉-Si₄U₂: C, 38.39; H, 7.31; N, 6.89. Found: C, 38.07; H, 7.01; N, 6.38.

X-ray Crystallographic Analysis of 2. A red, slab-shaped crystal was placed on a Bruker P4/CCD/PC diffractometer and cooled to 203 K using a Bruker LT-2 temperature device. The data were collected

- (23) Roussel, P.; Alcock, N. W.; Scott, P. *Inorg. Chem.* **1998**, 37, 3455.
 (24) Runde, W.; Neu, M. P.; Conradson, S. D.; Clark, D. L.; Palmer, P. D.; Reilly, S. D.; Scott, B. L. *Mater. Res. Soc. Symp. Proc.* **1997**, 465, 693.

Table 1. Crystallographic Data for [K(18-crown-6)(Et₂O)][UO(μ₂-NCH₂CH₂N(CH₂CH₂NSiBu^tMe₂)₂)₂ (2)

formula	C ₅₂ H ₁₁₈ KN ₈ O ₉ Si ₄ U ₂
fw	1627.06
cryst syst	triclinic
space group	<i>P</i> 1̄ (No. 2)
cell dimens	
<i>a</i> , Å	12.1144(6)
<i>b</i> , Å	12.6084(6)
<i>c</i> , Å	14.5072(7)
α, °	101.374(1)
β, °	103.757(1)
γ, °	109.340(1)
<i>V</i> , Å ³	1936.60(16)
<i>Z</i>	1
<i>D</i> _{calcd} , g cm ³	1.395
μ, mm ⁻¹	4.338
λ(MoKα), Å	0.71073
temp, °C	-71
reflections collected	10 212
independent reflections	7257
R1 ^a	0.0523
wR2	0.1359
GOF	1.295

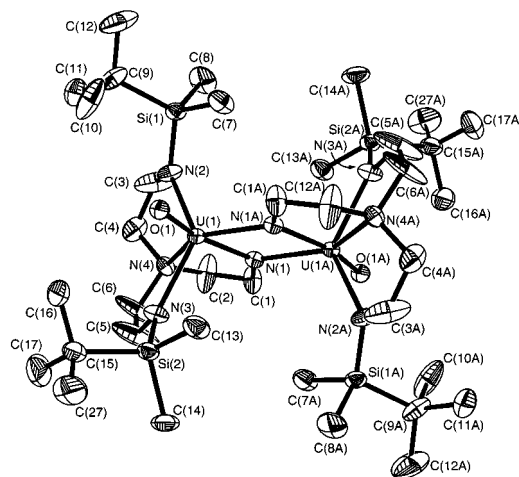
^a R1 = $\sum ||F_o| - |F_c|| / \sum |F_o|$ and wR2 = $[\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (0.0794P)^2]$.

using a sealed, graphite monochromatized MoKα X-ray source. A hemisphere of data was collected using a combination of ω and φ scans, with 20 s frame exposures and 0.3° frame widths. Data collection, initial indexing, and cell refinement were handled using SMART software.²⁵ Frame integration and final cell parameter calculation were carried out using SAINT software.²⁶ The data were corrected for absorption using the SADABS program.²⁷ Decay of reflection intensity was not observed.

The structure was solved in space group *P*1̄ (No. 2) using direct methods and difference Fourier techniques. The diethyl ether molecule was refined at one-half of the occupancy due to the small initial peak heights and no apparent disorder. Hydrogen atom positions were fixed (C–H = 0.98 Å for methylene and 0.96 Å for methyl). The hydrogen atoms were refined using the riding model, with isotropic temperature factors fixed to 1.5 (methyl) or 1.2 (methylene) 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 and converged with final residuals of R1 = 0.0444 and wR2 = 0.1307. Structure solution, refinement, graphics, and creation of publication materials were performed using SHELXTL NT.²⁸ Additional details of data collection and structure refinement are listed in Table 1.

Results and Discussion

Synthesis and Solid-State Molecular Structure of [K(18-crown-6)(Et₂O)][UO(μ₂-NCH₂CH₂N(CH₂CH₂NSiBu^tMe₂)₂)₂ (2). Addition of a THF solution of the triamidoamine ligand Li₃[N(CH₂CH₂NSiBu^tMe₂)₃] to a yellow slurry of the uranyl chloride complex [K(18-crown-6)]₂[UO₂(Cl)₄] (1) in THF, followed by workup of the reaction mixture in diethyl ether, yields reddish crystals of [K(18-crown-6)(Et₂O)][UO(μ₂-NCH₂CH₂N(CH₂CH₂NSiBu^tMe₂)₂)₂ (2) at -30 °C in moderate yield (44%). The reaction that produces 2 entails abstraction of the silyl group from one of the pendant amido nitrogen donors of the triamidoamine ligand along with the abstraction of one

**Figure 1.** Thermal ellipsoid drawing of the repeat unit of 2 showing the atom-labeling scheme used in the tables.**Table 2.** Selected Bond Lengths (Å) and Bond Angles (deg) for 2

U(1)–O(1)	1.838(5)	O(1)–U(1)–N(1)	161.2(2)
U(1)–N(1)	2.097(6)	O(1)–U(1)–N(2)	92.1(2)
U(1)–N(2)	2.334(6)	O(1)–U(1)–N(3)	92.9(2)
U(1)–N(3)	2.323(7)	O(1)–U(1)–N(1A)	87.2(2)
U(1)–N(4)	2.703(6)	O(1)–U(1)–N(4)	131.1(2)
U(1)–N(1A)	2.362(6)	N(2)–U(1)–N(1A)	118.6(2)
U(1)–U(1A)	3.5655(5)	N(3)–U(1)–N(1A)	116.9(2)
C(3)–C(4)	1.501(18)	U(1)–N(1)–U(1A)	106.0(2)
C(5)–C(6)	1.281(17)	C(1)–N(1)–U(1)	130.4(5)
N(1)–C(1)	1.453(9)	N(4)–U(1)–N(1)	67.8(2)
N(2)–C(3)	1.450(11)	Si(2)–N(3)–U(1)	123.6(4)
N(3)–C(5)	1.491(13)		

oxo group from the precursor uranyl complex. Spectroscopic examinations of the reaction byproducts have thus far been inconclusive with respect to identifying the fate of either leaving group. Nucleophilic attack at the N–Si bond of a triamidoamine ligand has been previously documented,²⁹ and U=O cleavage is a common reductive decomposition pathway of uranyl complexes. Further work is targeted at elucidating mechanistic information in the reaction that forms 2.

Single crystals of 2 suitable for X-ray diffraction were obtained by slow cooling of a concentrated diethyl ether 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 anion containing the atom numbering scheme used in the tables is shown in Figure 1. As there are no contacts observed between the counterions, the [K(18-crown-6)(Et₂O)] cation is omitted for clarity. The anion in 2 crystallographically manifests as a dimer, where each half is comprised of a uranium atom coordinated by a single terminal oxo ligand along with the capping amine N(4) and two of the three amido ligands (N(2) and N(3)) of the triamidoamine ligand. The third pendant amide of the tripodal ligand has been activated by the loss of the silyl substituent to give an imido group N(1), which forms an additional bridging interaction to the other uranium atom to produce the dimeric structure (with asymmetric bridging imido ligands). The overall negative charge for the dimer reveals 2 to formally be a U(V/VI) mixed-valence complex, and the structural equivalence between the two monomeric units, indicated by an inversion center at the midpoint of the U₂N₂ rhombus (the overall symmetry of the anion is idealized C_{2h}),

(25) SMART, 4.210; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 1996.

(26) SAINT, 4.05; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 1996.

(27) Sheldrick, G. SADABS, first release; University of Göttingen: Göttingen, Germany, 1996.

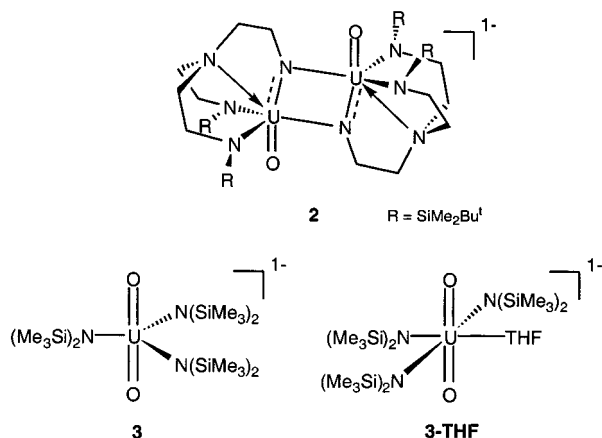
(28) SHELXTL NT, 5.10; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 1997.

(29) O'Donoghue, M. B.; Davis, W. M.; Schrock, R. R. *Inorg. Chem.* **1998**, *37*, 5149.

suggests there is no discernible way to assign separate oxidation states to either uranium center crystallographically.

The local coordination geometry about each uranium atom is that of a capped trigonal bipyramid. The oxo donor O(1) and the imido nitrogen atom N(1) comprise the axial ligands, and the two amido nitrogen atoms N(2) and N(3), together with the bridging imido donor N(1A), occupy the equatorial coordination sites. The amine nitrogen N(4) coordinates as the capping ligand. Axial distortion from idealized trigonal bipyramidal geometry is indicated by the O(1)–U(1)–N(1) angle of 162.1(2)° and is associated with the uranium–imido unit U(1)–N(1), as the axial U(1)–O(1) bond is approximately orthogonal (within 3°) to the three equatorial donors N(2), N(3), and N(1A). The deviation of the uranium–imido bond from trigonal bipyramidal geometry is evidently induced by a combination of the proximity of the capping amine donor N(4) (N(1)–U(1)–N(4) angle = 67.8(2)°) and the additional bridging interaction of N(1) to the other uranium atom U(1A). The U₂N₂ rhombus, the terminal oxo ligands, and the capping amine donors are all coplanar (within 2°).

The structure of **2** bears similarities to [Na(THF)₂][UO₂(N(SiMe₃)₂)₃] (**3**), a rare example of a uranyl complex with only three equatorial ligands recently reported from our laboratory (the overwhelming majority of uranyl complexes are coordinated by 4–6 ligands in the equatorial plane).⁷ First, the trans oxo–imido unit in **2** is isolobal to the trans dioxo group in **3**. Second, the three equatorial silylamido ligands in **3** may be equated in **2** with the two silylamido donors N(2) and N(3) and the bridging imido donor N(1A), as the U(1)–N(1A) bond distance of 2.362(6) Å is similar to the uranium–amido bond distances (average 2.32 Å). The main structural difference between **2** and **3** lies, therefore, in the presence of the amine donor N(4) in the tripodal ligand set in **2** which caps the trigonal bipyramid. It is possible for **3** to coordinate a neutral ligand as well;⁷ by NMR spectroscopy, it appears that the resulting adduct (**3-THF**) has the Lewis base occupying an equatorial position (geometric constraints of the tethered tripodal ligand in **2** preclude coordination of the amine N(4) in a strictly equatorial position).



The terminal U(1)–O(1) bond distance of 1.835(5) Å in oxo–imido **2** is long in comparison to the normal range of 1.76–1.79 Å observed in the majority of uranyl(VI) dioxo complexes.² This distance is comparable, however, to the terminal U=O bond lengths found in two other structurally characterized mono-oxo complexes.³⁰ Coincidentally, these examples include a U(V) oxo–aryloxide and a U(VI) oxo–imido species which provide structural comparisons not only with another uranium oxo–

imido derivative, but also for the two oxidation states (V and VI) represented in **2**. The U=O bond distance is 1.844(5) Å in the U(V) derivative (C₅Me₅)₂U(O)(O-2,6-Prⁱ₂-C₆H₃) and 1.860(6) Å in the U(VI) complex (C₅Me₅)₂U(O)(N-2,6-Prⁱ₂-C₆H₃). The long U=O distances in these complexes have been ascribed to the electron-rich environment at the metal center supplied by the (C₅Me₅)₂ ligand system and are supported by the low U=O stretching frequencies (near 755 cm⁻¹). The moderately lengthened U=O bond in **2**, along with a ν_{U=O} value of 827 cm⁻¹ obtained from the IR and Raman spectra, suggests a similar electron-rich environment supplied by the strong donor amido ligands. In comparison, in the oxo phosphorane–iminato complex [PPh₄][U(O)(NP(*m*-MeC₆H₄)₃)Cl₄],³¹ where electron-withdrawing chloro ligands predominate, the U=O bond distance of 1.759(13) Å is considerably shorter, and ν_{U=O} (850 cm⁻¹) is also higher.

There is a significant difference between the two U–N imido bond distances U(1)–N(1) and U(1A)–N(1) within the U₂N₂ unit in oxo–imido **2**. The U(1)–N(1) bond distance of 2.097(6) Å is indicative of metal–ligand multiple bonding from the imido nitrogen donor and is similar to previously reported terminal U–N imido bond lengths, which range from 1.85 to 2.07 Å.^{9,29,32–34} The comparatively longer U=N bond distance in **2** presumably arises because the ligand is not terminal but extends an additional bridging interaction to U(1A). The bridging U(1A)–N(1) bond distance of 2.362(6) Å is considerably longer; in fact, it is comparable to the uranium–amido bond lengths U(1)–N(2) and U(1)–N(3) at 2.334(6) and 2.323(7) Å, respectively. The asymmetry in the U–N imido interactions in the U₂N₂ moiety in **2** is typical for uranium complexes with bridging imido ligands,^{35,36} but the difference is more pronounced in **2**. For example, the shorter U–N distance generally ranges from 2.15 to 2.17 Å (in comparison to 2.10 Å in **2**), while the longer bridging U–N contact ranges between 2.23 and 2.31 Å (2.36 Å in **2**). Electronic arguments have been put forth to account for these asymmetric bridging interactions in uranium–imido complexes.³⁵

Amido ligands were employed in this work in an attempt to create an electron-rich environment capable of supporting a cis dioxo geometry. Despite the fact that this class of complexes was not isolated, the structure of **2** provides insight into the influence of the supporting ligands on metal–ligand multiple bonding. For the actinides, this genre is dominated by the extensive number of trans dioxo actinyl complexes. By comparison, there have been only two uranium examples reported thus far that contain the isolobal oxo–imido unit, a discrepancy that contrasts sharply with analogous transition metal chemistry where dioxo and oxo–imido derivatives are fairly equally represented.^{37–40} The only other known structurally character-

(31) Brown, D. R.; Denning, R. G.; Jones, R. H. *Chem. Commun.* **1994**, 2601.

(32) Brennan, J. G.; Andersen, R. A. *J. Am. Chem. Soc.* **1985**, *107*, 514.

(33) Zalkin, A.; Brennan, J. G.; Andersen, R. A. *Acta Crystallogr.* **1988**, *C44*, 1553.

(34) Burns, C. J.; Smith, W. H.; Huffman, J. C.; Sattelberger, A. P. *J. Am. Chem. Soc.* **1990**, *112*, 3237.

(35) Brennan, J. G.; Andersen, R. A.; Zalkin, A. *J. Am. Chem. Soc.* **1988**, *110*, 4554.

(36) Stewart, J. L.; Andersen, R. A. *New J. Chem.* **1995**, *19*, 587.

(37) Vaughan, W. M.; Abboud, K. A.; Boncella, J. M. *J. Organomet. Chem.* **1995**, *485*, 37.

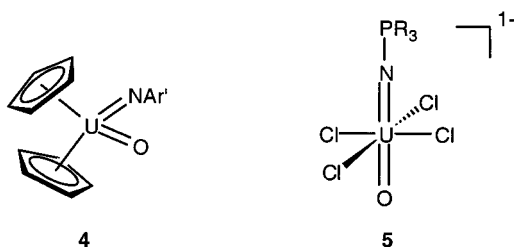
(38) Copley, R. C. B.; Dyer, P. W.; Gibson, V. C.; Howard, J. A. K.; Marshall, E. L.; Wang, W.; Whittle, B. *Polyhedron* **1996**, *15*, 3001.

(39) Galindo, A.; Montilla, F.; Pastor, A.; Carmona, E.; Gutiérrez-Puebla, E.; Monge, A.; Ruiz, C. *Inorg. Chem.* **1997**, *36*, 2379.

(40) Lee, S.-M.; Kowallick, R.; Marcaccio, M.; McCleverty, J. A.; Ward, M. D. *J. Chem. Soc., Dalton Trans.* **1998**, 3443.

(30) Arney, D. S. J.; Burns, C. J. *J. Am. Chem. Soc.* **1993**, *115*, 9840.

ized examples of uranium oxo–imido complexes in addition to **2** are the U(VI) metallocene complex (C_5Me_5)₂U(O)(N-2,6-*i*-Pr₂C₆H₃) (**4**) mentioned earlier³⁰ and the phosphorane–iminato derivative [PPh₄][U(O)(NP(*m*-MeC₆H₄)₃)Cl₄] (**5**) reported by Denning³¹ (other related analogues have recently been noted).⁴¹ The contrast in the respective geometries and bonding parameters between **4** and **5** is striking and provides useful comparisons with **2**. Whereas **4** possesses two multiply bonded ligands coordinating in *cis* positions along the metallocene wedge, **5** is essentially a uranyl analogue with *trans* oxo–imido functionalities. Also, the U=O and U=N bond distances in **4** are considerably lengthened at 1.844(4) and 1.988(4) Å, respectively, in comparison to 1.759(13) and 1.901(14) Å for the corresponding bond distances in **5**. Complex **2** shares features of both derivatives. As indicated before, there is a structural resemblance between **2** and the uranyl amido complex **3** which indicates a similar resemblance to **5** and lends further support for the ubiquitous nature of this linear structural entity in the actinides. However, the elongated U=O and U=N bond distances in **2** are ostensibly more in line with **4**, reflecting similar electronic environments despite the different geometries. This capacity to accommodate an electron-rich uranium center with different possible coordination geometries for metal–ligand multiple bonding has potential bearing for the future prospects of isolating a *cis* dioxo complex.



Mixed-Valent Complexes of Uranium: Electronic Delocalization? An interesting complication to this reaction is the one-electron reduction overall for the dinuclear product **2** relative to the starting uranyl(VI) species, resulting in a formally mixed-valent U(V/VI) species with one unpaired electron. Mixed-valent complexes of the f-elements are being reported with increasing frequency;^{42–46} nevertheless, the number of actinide derivatives comprises only a few uranium examples,^{18,47–49} and little mention has been made with respect to the degree of electronic delocalization in these systems. In the solid-state structure of **2** shown in Figure 1, there is an inversion center between the two units that make up the anion; hence, both uranium centers are equivalent crystallographically, suggesting an averaged U(5.5) oxidation state for each. The bridging imido nitrogen atoms in **2** are sp² planar, so time-independent delocalization of the single electron over the entire U₂N₂ unit is hypothetically possible

through orbital overlap between the nitrogen p-π orbital and metal-based orbitals (5f or 6d) of suitable symmetry. The NMR and EPR spectroscopic data are intriguing in this regard. The influence of the unpaired electron is conspicuous in the extreme paramagnetic broadening in the ¹H NMR spectrum of **2**, whereby the only resonances detected over the temperature range studied (–20 to 60 °C) are attributed to the [K(18-crown-6)-(Et₂O)] cation. This peak broadening varies little with temperature and is particularly notable given the separation between the two ions in the solid-state structure, with the likelihood that a similar spatial separation exists in solution. As NMR spectra for paramagnetic uranium(V) complexes, although broadened, are otherwise routinely observed, the absence of resonances associated with the dimeric anion of **2** is noteworthy, and other uranium mixed-valent complexes generated from our laboratory have yielded similarly broadened or NMR silent spectra.⁵⁰ Consistent with the inability to obtain a resolved paramagnetic ¹H NMR spectrum for **2** is the observation of strong EPR signals at 100 K, as the respective time scales associated with electron relaxation often render these two spectroscopic techniques mutually exclusive.⁵¹ In a toluene glass at 100 K, three signals are observed for **2**: $g_x = 6.22$, $g_y = 2.19$, $g_z = 1.21$. As with the anomalous difficulty in observing an NMR spectrum for **2**, the facility with which EPR peaks were detected contrasts with most uranium complexes possessing low symmetry, where measurements typically necessitate low temperatures of 15 K or lower. Both of these anomalies originate from the same process of electron relaxation, but whether this arises due to electronic delocalization across the imido bridges or rapid electron exchange between metal centers in **2** is uncertain.

Other supporting data that have been obtained do not clarify the extent and/or the time scale of valence localization in **2**. For example, an attempt to identify discrete (localized) or averaged (delocalized) oxidation states from the X-ray absorption near-edge structure (XANES) of a solid sample of **2** yielded inconclusive assignments. In the IR spectrum, two U=O stretches are predicted for a valence localized species if intramolecular electron transfer is slow on the IR time scale,^{52,53} but in **2**, a single U=O stretch is observed at 827 cm^{–1}, again suggesting valence averaging on a picosecond or faster time scale. For most transition metal mixed-valence systems, electronic transitions due to interelectronic transfer (IT bands) are typically observed in the NIR absorption spectrum.^{54,55} However, the optical spectrum obtained for **2** shows no such features in the NIR region, but instead the spectrum reveals a broad absorption band that extends from the UV to approximately 800 nm. Indeed, the actual features of such IT transitions are currently unknown for mixed-valent species of the f-elements.¹⁸ Interestingly, the absence of bands in the NIR is also notable in that f–f transitions are commonly observed in this region in U(V) complexes.

Finally, electrochemical studies conducted in THF solutions of **2** show a quasi-reversible reduction process [U(VI/V) + e[–] ⇌ U(V/V)] and a totally irreversible oxidation process [U(VI/V) ⇌ U(VI/VI) + e[–]]. The former occurs at ~–2.0 V vs NHE and the latter at ~–0.9 V vs NHE. Notably, the rest potential

(41) Williams, V. C.; Müller, M.; Leech, M. A.; Denning, R. G.; Green, M. L. H. *Inorg. Chem.* **2000**, *39*, 2538.

(42) Burns, C. J.; Berg, D. J.; Andersen, R. A. *Chem. Commun.* **1987**, 272.

(43) Deacon, G. B.; Gitlits, A.; Skelton, B. W.; White, A. H. *Chem. Commun.* **1999**, 1213.

(44) Morton, C.; Alcock, N. W.; Lees, M. R.; Munslow, I. J.; Sanders, C. J.; Scott, P. *J. Am. Chem. Soc.* **1999**, *121*, 11255.

(45) Dubé, T.; Gambarotta, S.; Yap, G. *Organometallics* **2000**, *19*, 817.

(46) Dubé, T.; Conoci, S.; Gambarotta, S.; Yap, G. P. A. *Organometallics* **2000**, *19*, 1182.

(47) Zozulin, A. J.; Moody, D. C.; Ryan, R. R. *Inorg. Chem.* **1982**, *21*, 3083.

(48) Cotton, F. A.; Marler, D. O.; Schwotzer, W. *Inorg. Chem.* **1984**, *23*, 4211.

(49) Ryan, R. R.; Salazar, K. V.; Sauer, N. N. *Inorg. Chim. Acta* **1987**, *162*, 221.

(50) Unpublished results.

(51) Lamar, G. N.; Horrocks, W. D.; Holm, R. H. *NMR of Paramagnetic Molecules*; Academic Press: New York, 1973.

(52) Ito, T.; Hamaguchi, T.; Nagino, H.; Yamaguchi, T.; Kido, H.; Zavarine, I. S.; Richmond, T.; Washington, J.; Kubiak, C. P. *J. Am. Chem. Soc.* **1999**, *121*, 4625.

(53) Atwood, C. G.; Geiger, W. E. *J. Am. Chem. Soc.* **2000**, *122*, 5477.

(54) Chen, P.; Meyer, T. J. *Chem. Rev.* **1998**, *98*, 1439.

(55) Demadis, K. D.; Neyhart, G. A.; Kober, E. M.; White, P. S.; Meyer, T. J. *Inorg. Chem.* **1999**, *38*, 5948.

for the cell was at ~ -1.5 V vs NHE. There are large uncertainties associated with these potential values because there appears to be chemical processes (e.g., ligand dissociation) coupled to each one and because, as noted in the Experimental Section, there seems to be some reaction with the ferrocene added in large excess at the end of the electrochemical experiment to calibrate the cell potentials. Peak current analyses versus scan rate did show that the number of electrons transferred in the reduction process was ~ 1.2 times the number transferred in the oxidation process, so it appears unlikely that the reduction wave involved wholesale reduction of both uranium centers to the tetravalent state. Despite the uncertainties in potential values for the reduction and oxidation processes, the approximate difference in potential between these processes (~ 1.1 V) can be used to estimate the intrinsic stability of the mixed-valent [U(VI/V)] state according to the comproportionation reaction $\text{U(VI/VI)} + \text{U(V/V)} \rightleftharpoons 2 \text{U(VI/V)}$.⁵⁶ The equilibrium constant for this reaction is estimated to be $\sim 10^{18}$, indicating a very strong energetic preference for **2**.

Conclusions

Reaction between a triamidoamine ligand and a uranyl (UO_2^{2+}) complex has resulted in the mutual activation of both the ligand and the dioxo unit of the uranyl ion to give the unusual mixed-valent uranium(V/VI) oxo-imido dimer **2**. The conclusion that emerges from this study is that **2** has a structural resemblance to the uranyl family of species, but it possesses a

relatively electron-rich uranium center more typically found in organometallic systems. NMR and EPR spectroscopic studies suggest possible delocalization of the single unpaired electron across the imido bridges between the two uranium centers, although insight into the rate of intramolecular electron transfer as probed by other spectroscopic methods has not been provided thus far. However, we have been able to isolate other uranium mixed-valent systems stabilized by triamidoamine ligand sets, and we plan to investigate further into the electronic structure in these systems.

Future work targeted toward a stable cis dioxo uranium complex is aimed at the modification of the triamidoamine ligand set to include substituents on the pendant amido donors that are less susceptible to activation under the reaction conditions used. Toward that end, uranyl amido complexes are being utilized in amine elimination reactions with protonated triamidoamine ligands to lower the possibility for reduction of the uranium(VI) center. Finally, other types of ligands that are capable of coordinating in a tripodal geometry are also being investigated.

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Supporting Information Available: An X-ray crystallographic file, in CIF format, for the structure determination of **2** is available. This material is available free of charge via the Internet at <http://pubs.acs.org>.

(56) Kaim, W.; Klein, A.; Glöckle, M. *Acc. Chem. Res.* **2000**, *33*, 755.