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# A Highly Reactive Uranium Complex Supported by the Calix[4]tetrapyrrole Tetraanion Affording Dinitrogen Cleavage, Solvent Deoxygenation, and Polysilanol Depolymerization**

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Glenn P. A. Yap

Pyrrole-based polyanions are versatile ligands for *f* block metals which have been proved capable of assembling large cluster structures and of substantially increasing the reactivity of their low-valent derivatives. This is especially evident in the chemistry of divalent samarium, where the utilization of tetra- and dipyrrolyl anions leads to a larger extent of dinitrogen reduction through interaction with four metal centers.[1,2] However, a complete breakage of the N–N bond, as observed in transition-metal chemistry,[3] has not been observed in lanthanide chemistry, despite the possibility of assembling high-nuclearity low-valent clusters.[4]

Trivalent and lower valence uranium complexes might be promising substrates for $N_2$-activation purposes. For example, trisamide derivatives have recently provided the first two examples of dinitrogen fixation in actinide chemistry,[5] while the only existing complex of a formally divalent uranium amide displays a rare $\mu,\pi$ coordination of toluene.[6] These studies suggest that a high level of reactivity may be expected for low-valent uranium compounds with N-donor-based ligands. In addition, the possibility of uranium exhibiting several oxidation states and of affording multielectron reductions makes its low-valent derivatives particularly desirable. Accordingly, a preliminary study has shown that a trivalent uranium tetrapyrrolide complex may perform different types of solvent fragmentation, C–H bond oxidative addition, and ligand isomerization.[7]

Herein, we describe the results of our attempts to prepare a highly reduced uranium complex, which results in a surprising variety of processes including dinitrogen cleavage, solvent deoxygenation, and polysilanol depolymerization.

The starting complex $[(Et_8\text{-calix[4]tetrapyrrole})U(dme)][K(dme)]$ (**1**, DME = 1,2-dimethoxyethane) was synthesized by using the procedure previously reported for the preparation of the cyclohexyl congener[7] by the direct reaction of $[UI_3(dme)_2]$ with the tetrapotassium salt of the $Et_8$-calix-[4]-tetrapyrrole ligand (Scheme 1). The crystalline compound, isolated upon cooling the solution in DME, was characterized by X-ray crystallography (see Supporting Information) and standard analytical techniques.

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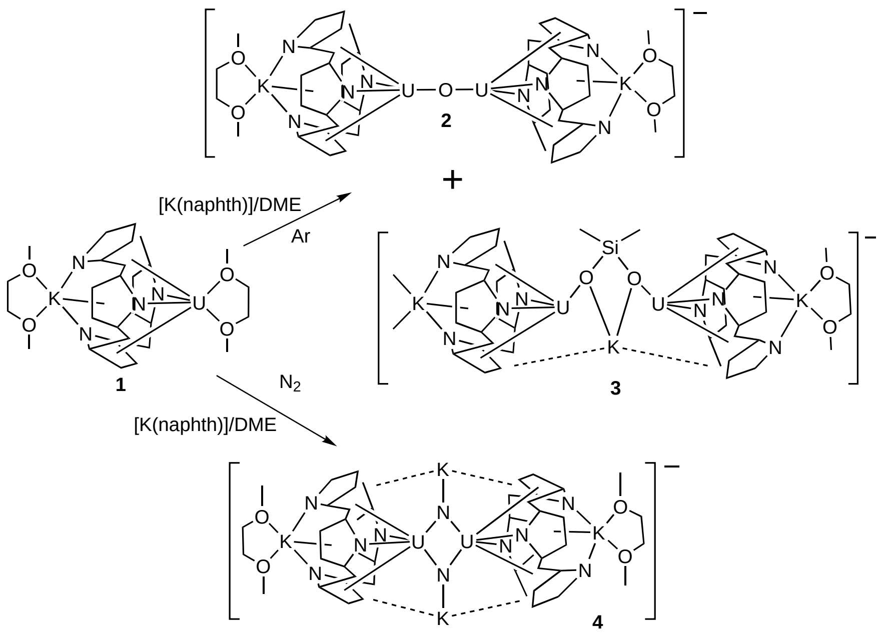

Scheme 1. Synthesis of **2**–**4**.

The reduction of the trivalent **1** with [K(naphthalenide)] carried out under Ar and in DME afforded a mixture of two different crystalline compounds. Manual separation of the crystalline mass under a microscope allowed the structural determination of the two species. In spite of the employment of a strong reducing agent, the first complex was a mixed-valence, dinuclear anionic $\mathrm{U^{III}/U^{IV}}$ $\mu$-oxo derivative [{K(dme)(calix[4]tetrapyrrole)U}$_2$($\mu$-O)][K(dme)$_4$] (**2**, Figure 1). Given the reproducibility of the reaction, the high yield and the stability of [K(naphthalenide)] solutions in DME, the formation of **2** is likely to be the result of a DME deoxygenation reaction performed by a transient intermediate. Furthermore, the presence of both methane and ethylene was clearly detected in the gas chromatogram of the reaction mixture, thus substantiating the proposal of DME fragmentation. The cleavage of DME, although rare, is not particularly surprising given the variety of THF fragmentation patterns displayed by tri- and tetravalent uranium complexes of a closely related ligand system.[7]

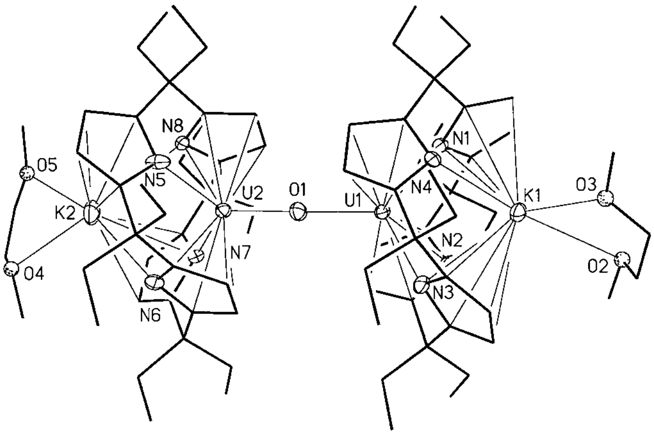

Figure 1. Thermal ellipsoid plot of the anionic moiety of **2**; bond lengths [Å] and angles [°]: U1-O1 2.226(10), U2-O1 2.017(10), U1-N1 2.539(12), U1-N2 2.748(11), U1-N3 2.542(12), U1-N4 2.757(10), K1-N1 3.072(11), K1-N3 3.200(12); U1-O1-U2 179.0(6).

The second product was even more unexpected. The crystal structure shows that the complex is the trivalent [[{K(dme)(calix[4]tetrapyrrole)U}($\mu$-Me$_2$SiO$_2$)($\mu$-K){U(calix[4]tetrapyrrole)K][K(dme)4]]$_n$ (**3**, Figure 2). This species is an infinite anionic polymer counterbalanced by discrete [K(dme)$_4$] cations. The polymer asymmetric unit consists of a dinuclear anion formed by two different [(calix[4]tetrapyrrole)UK] moieties bridged by Me$_2$SiO$_2$ and one potassium atom. In the first moiety the potassium atom is solvated by one DME molecule, while in the second moiety the potassium atom is connected to the pyrrolyl ring of another dinuclear unit, thus assembling the polymeric structure.

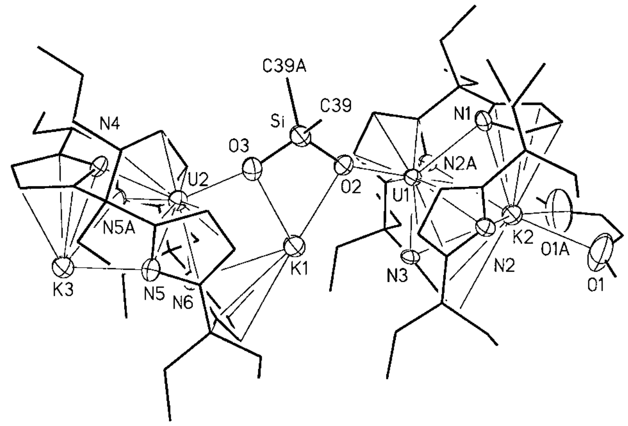

Figure 2. Thermal ellipsoid plot of the anionic moiety of **3**; bond lengths [Å] and angles [°]: U1-N1 2.555(19), U1-N2 2.724(12), U1-N3 2.541(16), U1-O2 2.178(15), U2-O3 2.20(15), K1-O2 2.727(15), K1-O3 2.819(16), O2-Si 1.627(15), O3-Si 1.586(17), K1-N6 3.047(18), K3-N4 3.060(18), K2-N2 3.05(14), K2-N3 3.258(18); O2-Si-O3 109.0(9), O2-K1-O3 56.2(5), U1-O2-Si 157.6(9), U2-O3-Si 16.5(10).

The trivalent state of **3** suggests that the complex was generated by the attack of a transient, highly reactive polysilanol species (silicon grease) which had contaminated the reaction flask. It is noteworthy that solutions of [K(naphthalenide)] in DME do not react with silicon grease over a long time period. As expected, reactions carried out without exposure to polysilanols yielded analytically pure **2** as the only detectable reaction product. This result was reproduced in six separate experiments.

Identical reactions carried out under dinitrogen afforded the unprecedented dinuclear, anionic $\mu$-nitrido $\mathrm{U^{V}/U^{IV}}$ mixed-valent complex, $[\{\mathrm{K(dme)(calix[4]tetrapyrrole)U}\}_2(\mu\text{-NK})_2][\mathrm{K(dme)_4}]$ (**4**) contaminated with small quantitites of **2**. Experiments carried out in Schlenk tubes, rather than in a $N_2$-filled dry-box, also gave **4** contaminated by a small amount of **2** as well as a variable amount of **3**. Analytically pure samples of **4** were conveniently obtained upon recrystallization of the crude crystalline mass from DME/hexane mixtures (61 % yield). Complex **4** is a symmetry-generated anionic dimer (Figure 3) consisting of two crystallographically identical [{[(calix[4]tetrapyrrole)U][K(dme)]}] moieties bridged by two K–N units. One potassium cation, solvated by four DME molecules and without bonding contacts with the anionic moiety, completes the asymmetric unit of the structure.

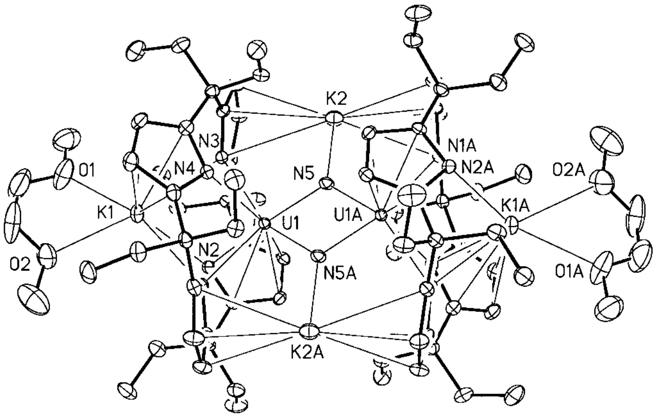

Figure 3. Thermal ellipsoid plot of the anionic moiety of **4**; bond lengths [Å] and angles [¤]: U1-N5 2.076(6), U1-N5A 2.099(5), U1-N1 2.665(5), U1-N2 2.899(6), U1-N3 2.697(5), U1-N4 2.612(5), U1-U2 3.3549(6), K2-N5 2.554(6); U1-N5-U1A 106.9(2), U1-N5-K2 124.8(3), N5-U1-N5A 73.1(2).

The fact that the structure is centrosymmetric might suggest the presence of a Class 1 mixed-valence uranium complex. On the other hand, it is possible that a Class 2 mixed-valence dimer, with two distinct $\mathrm{U^{IV}}$ and $\mathrm{U^{V}}$ metal centers, could exist with the two metals disordered over both positions, thus averaging the bond distances and angles. However, the presence of a pentavalent uranium center was conclusively proved from the near-IR spectrum, which clearly displays the characteristic absorption at 1247 nm,[8] and thus supports the idea that **4** might possess two chemically distinct metal centers. As expected for a uranium dimer with a short intermetallic contact,[9] the magnetic properties were uninformative. The complex is paramagnetic and displays a magnetic moment at room temperature that is lower than expected (3.41 $\mu_B$ per dimeric unit). The value of the magnetic moment drops with temperature to 1.91 $\mu_B$ at 2.5 K, with a flex at around 10 K that possibly indicates the presence of substantial antiferromagnetic coupling or superexchange.

A reaction carried out under $^{15}N_2$ gave the isotopically enriched derivative. Unfortunately, the paramagnetism of **4** destroyed both the $^{15}N$ and $^{14}N$ NMR spectra. However, the two crystalline compounds (with identical cell parameters) provided two strikingly different ESR spectra in solution at 100 K. While the unlabeled complex displayed a broad, single-line spectrum, the isotopically labeled derivative displayed a hyperfine structure consisting of 14 lines (see Supporting Information). These results in combination with the fact that **4** can only be reproducibly formed under an $N_2$ atmosphere (10 experiments) provide, together with the successful anisotropic refinement, satisfactory analytical data, and the near-IR spectrum, strong supporting evidence for identifying the bridging atoms as nitrides.

## *Experimental Section*

**1**: A solution of $[\mathrm{UI_3(dme)_2}]$ (3.1 g, 3.9 mmol) in DME (30 mL) was combined with a solution of $[(\mathrm{Et_8\text{-}calix[4]tetrapyrrole})\mathrm{K_4(dme)_2}]$ (3.4 g, 3.9 mmol) in the same solvent (30 mL). The resulting dark-green mixture was stirred for 4 h. Insoluble colorless material was removed from the solution by centrifugation and the resulting mother liquor was concentrated to about 15 mL. After the solution had stood for 24 h at room temperature, dark-green prisms of **1** were formed (3.1 g, 3.2 mmol, 82 %). Elemental analysis calcd (%) for $C_{44}H_{68}N_4O_4UK$: C 53.16, H 6.89, N 5.64; found: C 53.01, H 6.78, N 5.53; IR (Nujol mull): $\tilde{\nu} = 1604$(m), 1494(m), 1322(s), 1269(s), 1243(s), 1210(w), 1192(m), 1152(m), 1128(s), 1110(s), 1092(m), 1064(s), 1042(s), 1022(s), 976(m), 924(s), 886(s), 865(s), 772(s), 747(s), 730(s), 694(m), 618(m) $\mathrm{cm^{-1}}$. $\mu_{\mathrm{eff.}} = 2.80\,\mu_B$.

**2**: The following experiment was carried out in an Ar atmosphere in Schlenk glassware and with the joints lubricated with teflon grease (Krytox, DuPont). A solution of potassium naphthalenide was prepared from metallic K (0.06 g, 1.4 mmol) and naphthalene (0.18 g, 1.4 mmol) in DME (20 mL). The resulting dark-green solution was combined with a solution of **1** (1.4 g, 1.4 mmol) in DME (20 mL). The color of the reaction mixture changed instantly from dark-green to dark red-brown on stirring, which was continued for 4 h. The solution was concentrated to about 10 mL and layered with hexane (50 mL). After 3 days, dark red-brown prisms of **2** were formed (1.2 g, 0.5 mmol, 76 %). Elemental analysis calcd (%) for $C_{96}H_{156}N_8O_{13}U_2K_3$: C 51.85, H 7.07, N 5.04; found: C 51.77, H 6.98, N 4.96; IR (Nujol mull): $\tilde{\nu} = 1323$(m), 1261(s), 1192(w), 1157(w), 1089(s), 1022(s), 980(m), 925(m), 887(m), 853(m), 799(s), 764(m), 739(m), 650(s) $\mathrm{cm^{-1}}$. $\mu_{\mathrm{eff}} = 3.81\,\mu_B$.

**3**: The procedure was the same as for **2** but employing high-vacuum grease (Dow Corning). A dark-green solution of **1** (2.4 g, 2.5 mmol) in DME (20 mL) was mixed with a solution of potassium naphthalenide prepared from metallic K (0.10 g, 2.5 mmol) and naphthalene (0.3 g, 2.5 mmol) in DME (20 mL). After stirring for 4 h, the solution was concentrated to a volume of about 15 mL and layered with hexane (60 mL). After 2 days a mixture of dark red-brown crystals of **2** and dark-red prisms of **3** were formed (total yield 2.1 g). The manual separation of **3** for analytical purposes proved unfeasible in this case and no analytical characterization, other than X-ray structure determination, was possible. However, crystals of **2** could be manually separated under a microscope and identified by IR and by comparison of the crystallographic cell parameters.

**4**: The experiment was either carried out following a procedure identical to **2** but under an $N_2$ atmosphere or in a dry-box. In a typical dry-box experiment, a solution of potassium naphthalenide was prepared from metallic K (0.023 g, 0.59 mmol) and naphthalene (0.076 g, 0.59 mmol) in DME (7 mL). The solution was mixed with a solution of **1** (0.55 g, 0.55 mmol) in DME (10 mL). The reaction mixture immediately changed from dark-green to dark brown-red. Stirring was continued for 4 h at room temperature. The solution was then concentrated to a volume of about 4 mL and layered with hexane (10 mL). After 2 days, dark-orange crystals of **4** contaminated by a small amount of **2** were separated. Recrystallization of the crystalline mass from DME/hexane (4 mL/20 mL) yielded analytically pure dark-orange crystals of **4** (0.387 g, 0.17 mmol, 61 %). Elemental analysis calcd (%) for $C_{96}H_{156}N_{10}O_{12}U_2K_5$: C 49.83, H 6.80, N 6.05; found: C 49.78, H 6.77, N 6.01; IR (Nujol mull): $\tilde{\nu} = 1321$(m), 1269(m), 1245(s), 1207(w), 1189(m), 1128(m, br), 1086(s, br), 1042(m), 978(m), 921(m), 887(m), 851(s), 785(s), 739(s, br), 680(s), 673(s), 635(s) $\mathrm{cm^{-1}}$.

Crystal data. **1**: $C_{88}H_{136}N_8O_8K_2U_2$, $M_r = 1988.30$, orthorhombic, space group *Pbca*, $a = 13.226(3)$, $b = 21.313(7)$, $c = 31.827(11)$ Å, $V = 8972(5)$ Å$^3$, $Z = 8$, $\rho_{\mathrm{calcd}} = 1.472\ \mathrm{Mg\,m^{-3}}$, $\mu = 3.755\ \mathrm{mm^{-1}}$, $F(000) = 4024$, 26017 reflections collected, 9658 independent reflections, GOF = 1.049, $R = 0.0526$, $wR^2 = 0.1196$. **2**: $C_{96}H_{156}N_8O_{13}K_3U_2$, $M_r = 2223.65$, triclinic, space group $P\bar{1}$, $a = 17.325(1)$, $b = 18.258(1)$, $c = 19.616(2)$ Å, $\alpha = 108.527(2)$, $\beta = 90.998(2)$, $\gamma = 105.658(2)°$, $V = 5628.9(8)$ Å$^3$, $Z = 2$, $\rho_{calcd} = 1.312$ Mg m$^{-3}$, $\mu = 3.039$ mm$^{-1}$, $F(000) = 2266$, 44317 reflections collected, 16076 independent reflections, GOF = 1.021, $R = 0.0723$, $wR^2 = 0.1947$. **3**: $C_{94}H_{102}N_8O_{12}K_4SiU_2$, $M_r = 2196.34$, monoclinic, space group $P2_1/m$, $a = 16.322(1)$, $b = 17.691(2)$, $c = 19.772(2)$ Å, $\beta = 98.956(2)°$, $V = 5643.4(9)$ Å$^3$, $Z = 2$, $\rho_{calcd} = 1.293$ Mg m$^{-3}$, $\mu = 3.076$ mm$^{-1}$, $F(000) = 2184$, 44186 reflections collected, 6134 independent reflections, GOF = 1.058, $R = 0.0529$, $wR^2 = 0.1737$. **4**: $C_{96}H_{156}N_{10}O_{12}K_5U_2$, $M_r = 2313.87$, monoclinic, space group $P2_1/n$, $a = 13.111(1)$, $b = 22.953(3)$, $c = 17.976(2)$ Å, $\beta = 91.634(2)°$, $V = 5407(1)$ Å$^3$, $Z = 2$, $\rho_{calcd} = 1.421$ Mg m$^{-3}$. $\mu = 3.241$ mm$^{-1}$, $F(000) = 2354$, 12592 reflections collected, 6924 independent reflections, GOF = 1.002, $R = 0.0383$, $wR^2 = 0.0908$. CCDC-177345, -177346, -177347, -177348 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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# Are Ate Complexes True Intermediates in Lithium–Metalloid Exchange? Subtle Effects of Ion-Pair Structure in Lithium–Tellurium and Lithium–Selenium Exchange Reactions[**]

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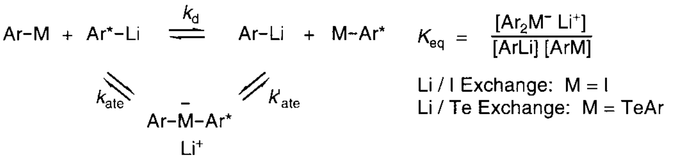
The lithium–metalloid exchange reaction is widely used to prepare synthetically valuable organolithium reagents. The full synthetic potential of one of the most important of these reactions, the Li/I exchange, was not realized (e.g., in the synthesis of alkyllithium reagents) until mechanistic studies showed that it was a well-behaved polar process without a significant radical component.[1a,b,2] Ate complexes, first proposed by Wittig and Schöllkopf,[3] are presumptive intermediates in these reactions [Eq. (1)]. Ate complexes of iodine,[1a,b,4] tellurium,[1b,5] selenium,[1c,5] tin,[1d,6] and silicon[7] having only alkyl and aryl ligands have been characterized in solution and in the solid state, and probed by high-level calculations.[8] Their presence, however, is not proof that they are intermediates in the exchange. No direct evidence has been reported for any Li/M exchange which shows that all of the exchange proceeds along path $k_{ate}$, and none by the direct exchange path $k_d$, which bypasses the ate complex [Eq. (1)]. To perform such an experiment with dynamic NMR (DNMR) spectroscopy, the three reactants (monomeric ArLi, ArM, and $Ar_2MLi$) in the triangular equilibrium of Equation (1) must be present in detectable concentrations under conditions for which the rates $k_d$, $k_{ate}$, and $k'_{ate}$ can each be measured.



(1)

A number of Li/I and Li/Te exchanges we investigated failed to provide a clear answer. Exchanges of PhI and $Ph_2Te$ with PhLi could not be analyzed because no solvent of appropriate polarity was found such that all species were detectable. In THF both monomer and dimer were observable, but the equilibrium constant $K_{eq}$ [Eq. (1)] for the ate complex was so high that insufficient PhLi and/or PhI/$Ph_2Te$ (whichever was stoichiometrically limiting) was present.[1b] In less polar, mixed solvents, the concentration of PhLi monomer was too low for proper line-shape analysis[1e,9] (the dimer of PhLi is not active in the exchange process[1b]). A problem which prevents kinetic analysis of Li/I exchanges is the fast reaction between ArI and the ate complex, in which the latter

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