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# U(IV) and U(V) azide complexes supported by amide or aryloxide ligands†

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Received 19th May 2009, Accepted 13th July 2009

First published as an Advance Article on the web 24th July 2009

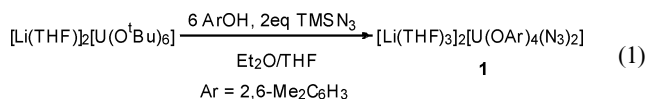
DOI: 10.1039/b909879h

The uranium(IV) azides  $[\text{Li}(\text{THF})_3]_2[\text{U}(\text{OAr})_4(\text{N}_3)_2]$ , Ar = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, and  $\{[\text{Na}(\text{THF})_4][\text{U}[\text{N}(\text{SiMe}_3)_2]_3(\text{N}_3)_2]\}_x$  have been synthesised and structurally characterised. Oxidation of these complexes affords  $[\text{Li}(\text{THF})_3][\text{U}(\text{OAr})_5(\text{N}_3)]$  and  $\text{U}[\text{N}(\text{SiMe}_3)_2]_3(\text{N}_3)_2$ , which are the first azides of U(V).

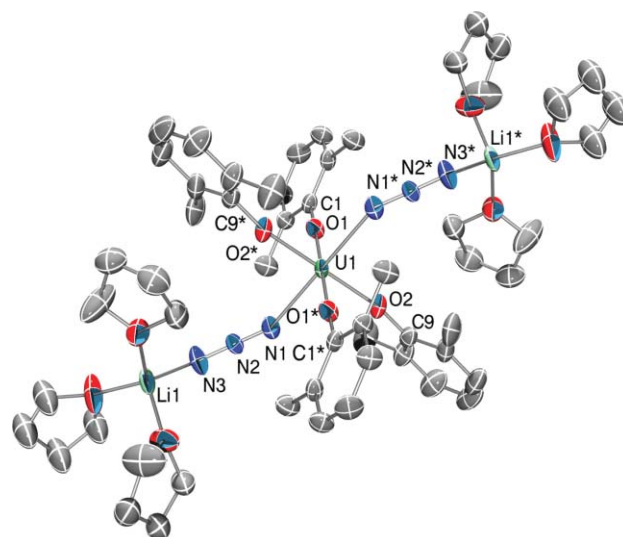
Metal azides are useful precursors for the synthesis of imido<sup>1–4</sup> and nitrido<sup>5,6</sup> complexes. This reactivity is particularly attractive for use in actinide chemistry as it offers a means of accessing metal–ligand multiple bonds. Probing the degree of covalency in actinide–ligand interactions is an active area of research,<sup>7–11</sup> and complexes possessing multiple bonds are useful for elucidating the extent of 6d- and 5f-orbital participation in bonding. Furthermore, azides offer a possible route to uranium nitride (UN), a potential fuel for Generation-IV nuclear power reactors.<sup>12–14</sup> However, only a few uranium nitride complexes are known.<sup>15–19</sup> Of these,  $[(\text{C}_5\text{Me}_5)_2\text{U}(\mu\text{-N})(\text{C}_5\text{Me}_5)_2]_4$ ,<sup>15</sup>  $[(\text{C}_5\text{Me}_5)_2\text{U}(\mu\text{-I})_2(\mu\text{-N})]_6$ ,<sup>16</sup>  $\{[\text{Cs}(\text{MeCN})_3][\text{U}_4(\mu\text{-N})_8(\mu\text{-N}_3)_8(\text{MeCN})_8\text{I}_6]\}_x$ ,<sup>17</sup> and  $(\text{C}_6\text{F}_5)_3\text{BN}\equiv\text{U}[\text{N}^+(\text{t}\text{Bu})(3,5\text{-Me}_2\text{C}_6\text{H}_3)]_3$ <sup>19</sup> were synthesised from azide precursors, illustrating the utility of azides to generate uranium nitrido complexes. To this end, we have synthesised a series of uranium azide complexes, including the first reported azides of uranium(V).

Alcoholysis of  $[\text{Li}(\text{THF})_2][\text{U}(\text{O}^t\text{Bu})_6]$  with 6 equiv. ArOH (Ar = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) in the presence of 2 equiv. Me<sub>3</sub>SiN<sub>3</sub> generates the U(IV) bis(azide),  $[\text{Li}(\text{THF})_3]_2[\text{U}(\text{OAr})_4(\text{N}_3)_2]$  (**1**), in moderate yield (eqn (1)).<sup>20</sup> The reaction is likely driven by the formation of strong Si–O bonds, presumably yielding either Me<sub>3</sub>SiO<sup>+</sup>tBu or Me<sub>3</sub>SiOAr as by-products. The <sup>1</sup>H NMR spectrum of **1** in C<sub>6</sub>D<sub>6</sub> consists of three broad peaks at 8.86, 12.26, and 14.12 ppm in a 3 : 1 : 2 ratio, respectively, assignable to the aryloxide ligands. A very broad resonance is also observed at –3.75 ppm, assignable to coordinated THF.

Recrystallisation of **1** from hexanes/Et<sub>2</sub>O provides colourless material suitable for X-ray crystallographic analysis.‡ Complex **1** crystallises in the monoclinic space group  $P2_1/n$ ,



and its solid-state molecular structure is shown in Fig. 1. The octahedral uranium centre is coordinated by four aryloxide ligands and two *trans*-azido ligands. Complex **1** exhibits a U–N<sub>azide</sub> bond length of U1–N1 = 2.442(6) Å and a U–N<sub>α</sub>–N<sub>β</sub> bond angle of U1–N1–N2 = 141.9(4)°. These parameters fall within the



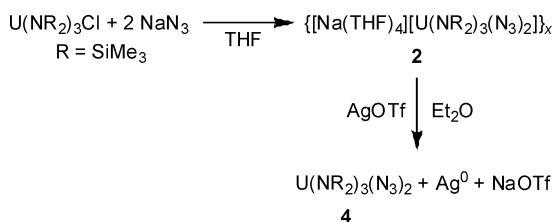
**Fig. 1** ORTEP diagram of  $[\text{Li}(\text{THF})_3]_2[\text{U}(\text{OAr})_4(\text{N}_3)_2]$  (**1**) with 50% probability ellipsoids. Asterisks indicate symmetry related atoms. Selected bond lengths (Å) and angles (°): U1–N1 = 2.442(6), U1–O1 = 2.191(4), U1–O2 = 2.169(4), N1–N2 = 1.181(8), N2–N3 = 1.173(8), Li1–N3 = 2.02(1), U–N1–N2 = 141.9(4), U–O1–C1 = 175.6(3), U1–O2–C9 = 168.7(4), N1–N2–N3 = 177.6(7), O1–U1–O2 = 90.1(1), N1–U1–O1 = 91.1(2), N1–U1–O2 = 90.2(7).

range of other structurally characterised uranium azides, which display U–N<sub>azide</sub> bond distances and U–N<sub>α</sub>–N<sub>β</sub> bond angles of 2.219(6)–2.564(12) Å and 121.5(5)–178.6(7)°, respectively.<sup>15,17,21–25</sup> The azide moiety of **1** is linear (N1–N2–N3 = 177.6(7)°) and it exhibits symmetrical N–N distances (N1–N2 = 1.181(8) Å, N2–N3 = 1.173(8) Å). These equivalent N–N distances are suggestive of a largely ionic U–N<sub>azide</sub> interaction,<sup>26–28</sup> and they differ from those observed in the uranium heptaazide  $[\text{Bu}_4\text{N}][\text{U}(\text{N}_3)_7]$  (av. N<sub>α</sub>–N<sub>β</sub> = 1.20 Å; N<sub>β</sub>–N<sub>γ</sub> = 1.10 Å),<sup>22</sup> which may possess U–N<sub>azide</sub> interactions with larger covalent character. The Li–N<sub>azide</sub> distance (Li–N<sub>3</sub> = 2.02(1) Å) is comparable to other Li–N<sub>azide</sub> bond lengths.<sup>29,30</sup> Lewis acid coordination to the azide moiety could potentially induce nitrogen elimination,<sup>31</sup> but in complex **1** coordination of Li<sup>+</sup> to the N<sub>3</sub><sup>–</sup> unit does not give rise to this mode of reactivity.

We have also synthesised an amide-supported U(IV) azide complex. Addition of excess NaN<sub>3</sub> to a THF solution of  $\text{UCl}[\text{N}(\text{SiMe}_3)_2]_3$ <sup>32</sup> produces a pink suspension after 24 h. Filtration of the mixture and recrystallisation from hexanes/THF affords  $\{[\text{Na}(\text{THF})_4][\text{U}[\text{N}(\text{SiMe}_3)_2]_3(\text{N}_3)_2]\}_x$  (**2**) as pink crystals in 54% yield (Scheme 1). The <sup>1</sup>H NMR spectrum of **2** in C<sub>6</sub>D<sub>6</sub>/CD<sub>2</sub>Cl<sub>2</sub> exhibits a broad resonance at –4.25 ppm, corresponding to the methyl protons of the amide ligand.

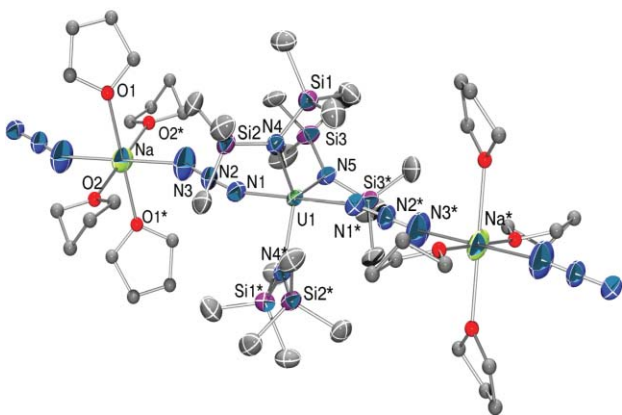
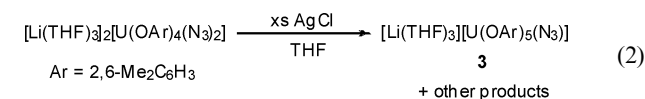
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† Electronic supplementary information (ESI) available: Experimental details. CCDC reference numbers 733176–733179. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b909879h



Scheme 1

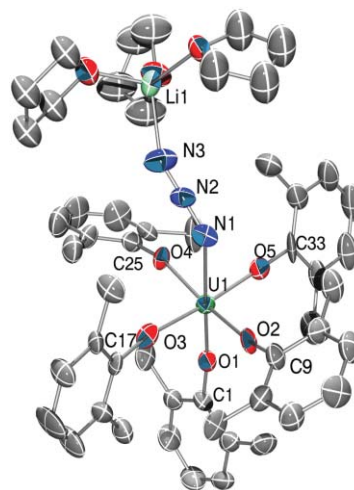
In the solid-state, **2** crystallizes in the monoclinic space group  $C2/c$  as a 1D coordination polymer (Fig. 2). Each uranium centre is trigonal bipyramidal and coordinated by three equatorial amido ligands and two axial azide ligands. The repeating unit is linked by a sodium cation which bridges two azide ligands. The U–N<sub>azide</sub> distance (U1–N1 = 2.337(6) Å) is notably shorter than that of **1** but comparable to other U<sup>IV</sup>–N<sub>azide</sub> bond lengths.<sup>15,17,21–24</sup> Complex **2** also exhibits a large U–N<sub>α</sub>–N<sub>β</sub> bond angle (U1–N1–N2 = 163.9(5)°). The metrical parameters of the azide ligands in **2** (N1–N2 = 1.175(7) Å, N2–N3 = 1.146(9) Å; N1–N2–N3 = 176.7(8)°) are comparable to those found in **1**, and the Na–N<sub>azide</sub> distance (Na–N3 = 2.408(8) Å) is consistent with other reported Na–N<sub>azide</sub> bond lengths.<sup>33,34</sup>



**Fig. 2** ORTEP diagram of  $\{\text{[Na(THF)}_4\text{[U[N(SiMe}_3)_2\text{]}_3(\text{N}_3)_2]\}_x$  (**2**) with 50% probability ellipsoids. Selected bond lengths (Å) and angles (°): U1–N1 = 2.337(6), U1–N4 = 2.274(4), U1–N5 = 2.272(7), N1–N2 = 1.175(7), N2–N3 = 1.146(9), Na–N3 = 2.408(8), U1–N1–N2 = 163.9(5), N1–N2–N3 = 176.7(8), N4–U1–N5 = 118.5(1), N1–U1–N4 = 91.0(2), N1–U1–N5 = 90.6(1).

It has recently been demonstrated that oxidation of a metal azide can elicit nitride formation.<sup>35</sup> Following this strategy, a solution of **1** in THF was treated with excess AgCl (eqn (2)). The reaction mixture immediately turns deep red, concomitant with gas evolution. As indicated by <sup>1</sup>H NMR spectroscopy, the reaction generates a mixture of products, however we were able to isolate a few red crystals in low yield. Characterisation of this material by X-ray crystallography reveals the formation of a U(v) azide complex  $\text{[Li(THF)}_3\text{]}_3\text{[U(OAr)}_5\text{(N}_3)_3\text{]}$  (**3**), the result of a 1e<sup>–</sup> oxidation of **1** and exchange of an azido group for an aryloxide.

Complex **3** crystallises in the orthorhombic space group  $P2_12_12_1$ , and its solid-state molecular structure is shown in Fig. 3. This species exhibits an octahedral uranium centre ligated by one azide and five aryloxide ligands. The U–N<sub>azide</sub> distance (U1–N1 = 2.318(8) Å) is shorter than that observed in **1**, consistent with a smaller U<sup>5+</sup> ionic radius. The U–N<sub>α</sub>–N<sub>β</sub> bond angle of **3** (U–N1–N2 = 129.4(6)°) is also considerably smaller than that observed in **1**. Oxidation of **1** to **3** does not affect the parameters of the azide moiety. The N–N distances of the azide ligand in **3** remain symmetrical (N1–N2 = 1.17(1) Å, N2–N3 = 1.15(1) Å) with a linear N–N–N bond angle (N1–N2–N3 = 176.7(9)°). The Li–N<sub>azide</sub> distance (Li1–N3 = 2.02(2) Å) is also similar to that in **1**.

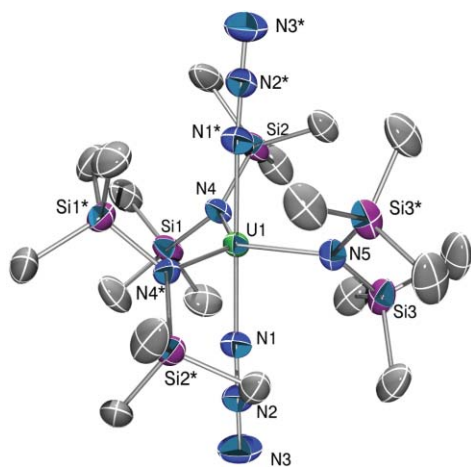


**Fig. 3** ORTEP diagram of  $\text{[Li(THF)}_3\text{]}_3\text{[U(OAr)}_5\text{(N}_3)_3\text{]}$  (**3**) with 50% probability ellipsoids. Selected bond lengths (Å) and angles (°): U1–N1 = 2.318(8), U1–O1 = 2.092(7), U1–O2 = 2.118(5), U1–O3 = 2.109(7), U1–O4 = 2.122(5), U1–O5 = 2.098(6), N1–N2 = 1.17(1), N2–N3 = 1.15(1), Li1–N3 = 2.02(2), U–N1–N2 = 129.4(6), U–O1–C1 = 170.4(6), U1–O2–C9 = 168.3(8), U1–O3–C17 = 168.5(6), U1–O4–C25 = 164.1(6), U1–O5–C33 = 175.0(6), N1–N2–N3 = 176.7(9), N1–U1–O2 = 83.8(3), O1–U1–O2 = 95.9(3), O2–U1–O3 = 88.8(2), O2–U1–O4 = 167.7(3), O2–U1–O5 = 92.8(2).

The <sup>1</sup>H NMR spectrum of **3** in C<sub>6</sub>D<sub>6</sub> is consistent with its solid-state molecular structure. The spectrum exhibits three peaks at 3.13, 5.64, and 8.32 ppm in a 3 : 1 : 2 ratio, respectively, assignable to the equatorial aryloxide ligands. A second set of resonances, also in a 3 : 1 : 2 ratio, is observed at 2.11, 5.33, and 7.68 ppm, respectively, assignable to the axial aryloxide ligand. The relative ratio between the these two peak sets is 4 : 1.

We have also investigated the oxidation of complex **2**. Addition of AgOTf to an Et<sub>2</sub>O suspension of **2** results in the rapid formation of a deep-red solution, but no obvious gas evolution (Scheme 1). Recrystallization from hexanes yields dark red crystals in good yield, and characterisation of this material by <sup>1</sup>H NMR spectroscopy and X-ray crystallography indicates the formation of  $\text{U[N(SiMe}_3)_2\text{]}_3(\text{N}_3)_2$  (**4**). Complex **4** is thermally stable and we see no evidence that it undergoes disproportionation.

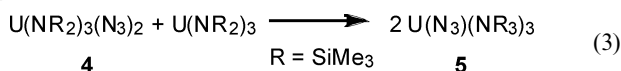
In the solid-state, **4** exhibits a trigonal bipyramidal coordination geometry (Fig. 4). As anticipated, the U–N<sub>azide</sub> bond length (U1–N1 = 2.226(3) Å) is shorter than that observed in **2**, while the U–N<sub>α</sub>–N<sub>β</sub> bond angle in **4** (U1–N1–N2 = 175.5(2)°) approaches linearity. Unlike complexes **1–3**, the N–N distances in **4** are no



**Fig. 4** ORTEP diagram of  $U[N(SiMe_3)_2]_3(N_3)_2 \cdot C_6H_{14}$  (**4**· $C_6H_{14}$ ) with 50% probability ellipsoids. Selected bond lengths (Å) and angles (°): U1–N1 = 2.226(3), U1–N4 = 2.166(2), U1–N5 = 2.168(3), N1–N2 = 1.190(4), N2–N3 = 1.136(5), U1–N1–N2 = 175.5(2), N1–N2–N3 = 179.5(4), N4–U1–N5 = 116.61(6), N1–U1–N4 = 90.55(9), N1–U1–N5 = 89.70(7).

longer equivalent (N1–N2 = 1.190(4) Å, N2–N3 = 1.136(5) Å), indicative of slight activation of the azide moiety.

In addition to exploring their oxidation, we have also probed the reduction chemistry of our azide complexes.  $U^{3+}$  is a powerful reducing agent<sup>36</sup> and is capable of reducing azides.<sup>17</sup> However, addition of  $U^{III}[N(SiMe_3)_2]_3$ <sup>37</sup> to **4** does not induce  $N_2$  elimination, instead its results in conproportionation, affording the previously prepared U(IV)



azide  $(N_3)U[N(SiMe_3)_2]_3$  (**5**) (eqn (3)).<sup>38</sup> Likewise, addition of Na/Hg amalgam to a THF solution of **2** fails to induce  $N_2$  elimination. In fact, no reaction is observed between these two reagents.

In summary, we have synthesized and structurally characterised a series of U(IV) and U(V) azide complexes supported by aryloxide and amide ligands. These complexes exhibit unique redox chemistry which we are continuing to investigate, with the intent of producing nitrido complexes of uranium.

## Notes and references

† Crystal data for **1**:  $C_{56}H_{84}Li_2N_6O_{10}U$ ,  $M = 1253.20$ , monoclinic, space group  $P2_1/n$ ,  $a = 11.4965(8)$  Å,  $b = 22.525(2)$  Å,  $c = 12.6040(9)$  Å,  $\beta = 114.922(2)^\circ$ ,  $V = 2959.9(4)$  Å<sup>3</sup>,  $Z = 2$ ,  $T = 150(2)$  K,  $\lambda = 0.71073$  Å,  $R_{int} = 0.1679$ ; a total of 23 433 reflections collected in the range  $2.15 < \theta < 27.10$ , of which 6184 were unique. GOF = 0.904,  $R_1 = 0.0438$  [for 3802 reflections with  $I > 2\sigma(I)$ ] and  $wR_2 = 0.1214$  (for all data). Crystal data for **2**:  $C_{34}H_{86}N_9NaO_4Si_6U$ ,  $M = 1114.68$ , monoclinic, space group  $C2/c$ ,  $a = 19.425(1)$  Å,  $b = 11.8336(8)$  Å,  $c = 25.319(2)$  Å,  $\beta = 104.369(2)^\circ$ ,  $V = 5637.8(7)$  Å<sup>3</sup>,  $Z = 4$ ,  $T = 150(2)$  K,  $\lambda = 0.71073$  Å,  $R_{int} = 0.1600$ ; a total of 23 319 reflections collected in the range  $2.03 < \theta < 26.37$ , of which 5716 were unique. GOF = 1.011,  $R_1 = 0.0483$  [for 4793 reflections with  $I > 2\sigma(I)$ ] and  $wR_2 = 0.1209$  (for all data). Crystal data for **3**:  $C_{52}H_{69}LiN_3O_8U$ ,  $M = 1109.07$ , orthorhombic, space group  $P2_12_12_1$ ,  $a = 12.525(1)$  Å,  $b = 20.098(2)$  Å,  $c = 20.536(2)$  Å,  $V = 5170(1)$  Å<sup>3</sup>,  $Z = 4$ ,  $T = 150(2)$  K,  $\lambda = 0.71073$  Å,  $R_{int} = 0.1611$ ; a total of 42 047 reflections collected in the

range  $1.42 < \theta < 27.10$ , of which 11 085 were unique. GOF = 0.940,  $R_1 = 0.0538$  [for 7010 reflections with  $I > 2\sigma(I)$ ] and  $wR_2 = 0.1255$  (for all data). Crystal data for **4**· $C_6H_{14}$ :  $C_{24}H_{48}N_9Si_6U$ ,  $M = 889.44$ , monoclinic, space group  $C2/c$ ,  $a = 18.767(1)$  Å,  $b = 14.6497(8)$  Å,  $c = 16.8791(9)$  Å,  $\beta = 111.295(2)^\circ$ ,  $V = 4323.7(4)$  Å<sup>3</sup>,  $Z = 4$ ,  $T = 150(2)$  K,  $\lambda = 0.71073$  Å,  $R_{int} = 0.0540$ ; a total of 17 620 reflections collected in the range  $1.81 < \theta < 26.73$ , of which 4513 were unique. GOF = 1.011,  $R_1 = 0.0243$  [for 4016 reflections with  $I > 2\sigma(I)$ ] and  $wR_2 = 0.0581$  (for all data).

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