Synthesis and Structure of High-Valent Organouranium Complexes Containing Terminal Monooxo Functional Groups

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Among the multiply bound functional groups in the d-elements, the oxo ligand has been known the longest and its chemistry most extensively developed.[1] Although the chemistry of the *trans*-dioxo actinyl ion $(AnO_2)^{n+}$ is well developed,[2] no examples of molecular compounds of the f-elements containing single terminal oxo functional groups exist, precluding investigation of the structural properties and reactivity of this functional group. Less is known about the properties of the uranium(V) oxo complexes; even the dioxo species $(UO_2)^+$ has only been studied to a limited extent due to its inherent instability.[2] This paucity of information is disappointing in light of the potential importance of the chemical behavior (such as basicity and lability) of oxo functional groups in determining the aggregation of actinide complexes in solution and the condensation and precipitation of ceramics. Here we describe the synthesis by oxidative atom-transfer chemistry and structure of organouranium(V) and -(VI) complexes containing terminal oxo functional groups of the general formula $(C_5Me_5)_2U$-$(EAr)(O)$ (E = O (3) and N (4); Ar = 2,6-diisopropylphenyl).

We recently reported the synthesis of $(C_5Me_5)_2U(NC_6H_5)_2$ by the two-electron oxidation of a monoimido precursor utilizing an organic azide.[3] In an effort to extend this synthetic methodology for the introduction of other functional groups, we investigated the utility of amine *N*-oxides as two-electron oxidants. The reaction of bright green $(C_5Me_5)_2UI(THF)$[4] with 1 equiv of KOAr (Ar = 2,6-diisopropylphenyl) in THF (initiated at ca. −10 °C and then allowed to warm to room temperature, 18 h) forms $(C_5Me_5)_2U(OAr)(THF)$ (1) in 75% yield as a dark green powder (eq 1).[5] The reaction of $(C_5Me_5)_2UMe_2$[6] with 1 equiv of H_2NAr in THF (70 °C, 24 h) forms $(C_5Me_5)_2U(NAr)(THF)$ (2) in 65% yield as an orange green powder (eq 2).[7]

$$(C_5Me_5)_2UI(THF) + 1KO\text{-}2,6\text{-}^iPr_2\text{-}C_6H_3 \xrightarrow[-KI]{THF}$$

$$(C_5Me_5)_2U(O\text{-}2,6\text{-}^iPr_2\text{-}C_6H_3)(THF) \quad (1)$$
$$(1)$$

$$(C_5Me_5)_2UMe_2 + 1NH_2\text{-}2,6\text{-}^iPr_2\text{-}C_6H_3 \xrightarrow[-2CH_4]{THF/\Delta}$$

$$(C_5Me_5)_2U(N\text{-}2,6\text{-}^iPr_2\text{-}C_6H_3)(THF) \quad (2)$$
$$(2)$$

The addition of 1 equiv of pyridine *N*-oxide to a stirred solution of 1 or 2 in THF at room temperature results in a rapid color change to black-brown. After 12 h the solvent is removed, yielding a black powder which is extracted and filtered twice through Celite, first in hexanes and then in hexamethyldisiloxane. Removal of the solvent yields pure $(C_5Me_5)_2U(E\text{-}2,6\text{-}^iPr_2\text{-}C_6H_3)$-$(O)$ (E = O (3) and N (4)) as black (3) or black-green (4) powders in 70% (3) and 65% (4) yields, respectively (eq 3).[8] Compounds 3 and 4 are highly soluble in all solvents and exhibit only modest air and moisture sensitivity.

$$(C_5Me_5)_2U(E\text{-}2,6\text{-}^iPr_2\text{-}C_6H_3)(THF) + 1C_5H_5NO \xrightarrow[-C_5H_5N]{THF}$$
$$E = O, 1; N, 2$$

$$(C_5Me_5)_2U(E\text{-}2,6\text{-}^iPr_2\text{-}C_6H_3)(O) \quad (3)$$
$$E = O, 3; N, 4$$

Single crystals of 3 and 4 were grown from concentrated hexane solutions at −40 °C and their structures determined from diffraction data collected at −80 °C (Figure 1). In the solid state, both 3 and 4 are shown to be monomeric and possess a single terminally bound oxo ligand. The U–C_{ring} distances for 3 and 4 are not significantly different (U(1)–C_{ring} range = 2.712-(8)–2.811(8) Å (3) and 2.730(6)–2.805(6) Å (4)) and are comparable to those observed in $(C_5Me_5)_2U(NC_6H_5)_2$ as well as in structurally characterized bis(pentamethylcyclopentadienyl)-uranium(IV) compounds.[3,10] The Cp*(centroid)–U(1)–Cp* angles of 134.1° (3) and 135.9° (4) are typical for those found in other Cp*$_2$UX$_2$ complexes.[10] The uranium–aryloxide oxygen

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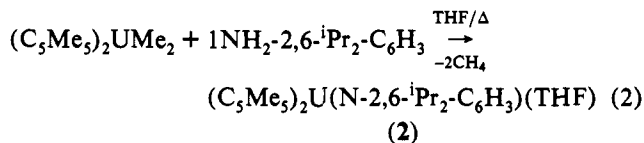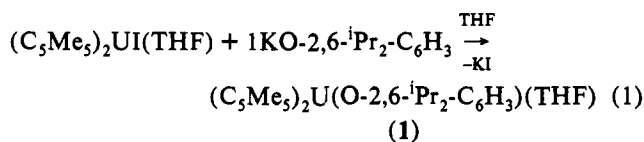
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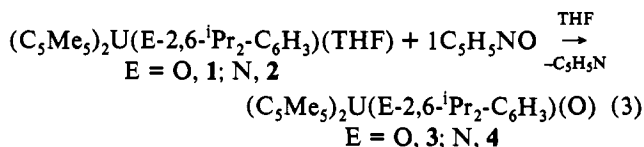
(5) $(C_5Me_5)_2U(OAr)(THF)$ (1): ^1H NMR (250 MHz, C_6D_6, 25 °C), δ 8.43 (s, $\nu_{1/2}$ = 50 Hz, 2 H), 7.71 (s, $\nu_{1/2}$ = 50 Hz, 1 H, para), −3.87 (s, $\nu_{1/2}$ = 50 Hz, 30 H, C$_5$Me$_5$), 6.27 (s, $\nu_{1/2}$ = 50 Hz, 12 H, CH*Me*$_2$), −14.98 (s, $\nu_{1/2}$ = 50 Hz, 4 H, THF), −21.80 (s, $\nu_{1/2}$ = 150 Hz, 2 H), −39.06 (s, $\nu_{1/2}$ = 75 Hz, 4 H, THF); IR (Nujol mull) 1590 (m), 1454 (sh), 1432 (vs), 1358 (m), 1324 (s), 1256 (vs), 1202 (s), 1145 (w), 1114 (w), 1100 (m), 1042 (m), 1017 (s), 934 (w), 920 (wbr), 885 (m), 867 (m), 851 (s), 803 (w), 791 (w), 745 (s), 726 (m), 692 (m), 565 (m) cm^{-1}. Anal. Calcd for $C_{36}H_{55}O_2U$: C, 57.01; H, 7.26. Found: C, 56.81; H, 7.39.

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(7) 2: ^1H NMR (250 MHz, C_6D_6, 25 °C) δ 39.39 (s, $\nu_{1/2}$ = 125 Hz, 2 H), 33.61 (s, $\nu_{1/2}$ = 240 Hz, 2 H), 17.13 (s, $\nu_{1/2}$ = 60 Hz, 1 H, para), 6.85 (s, $\nu_{1/2}$ = 60 Hz, 12 H, CH*Me*$_2$), −2.11 (s, $\nu_{1/2}$ = 60 Hz, 30 H, C$_5$Me$_5$), −17.02 (s, $\nu_{1/2}$ = 80 Hz, 4 H, THF), −32.01 (s, $\nu_{1/2}$ = 120 Hz, 4 H, THF); IR (Nujol mull) 1584 (m), 1457 (sbr), 1414 (s), 1357 (m), 1329 (sh), 1312 (s), 1256 (s), 1245 (vs), 1224 (m), 1209 (m), 1171 (w), 1155 (w), 1143 (m), 1118 (w), 1105 (m), 1054 (w), 1043 (w), 1016 (m), 934 (wsh), 914 (s), 864 (m), 855 (msh), 836 (w), 805 (w), 794 (w), 745 (s), 733 (w), 728 (w), 717 (w), 694 (w), 669 (wbr) cm^{-1}. Anal. Calcd for $C_{36}H_{55}NOU$: C, 57.21; H, 7.33; N, 1.85. Found: C, 56.93; H, 7.53; N, 1.53.

(8) ^1H NMR (250 MHz, C_6D_6, 25 °C): 3, δ 40.49 (s, $\nu_{1/2}$ = 125 Hz, 1 H), 12.78 (s, $\nu_{1/2}$ = 60 Hz, 1 H), 9.46 (s, $\nu_{1/2}$ = 80 Hz, 6 H, CH*Me*$_2$), 5.25 (s, $\nu_{1/2}$ = 60 Hz, 1 H), 4.77 (s, $\nu_{1/2}$ = 60 Hz, 1 H), 4.45 (s, $\nu_{1/2}$ = 100 Hz, 30 H, C$_5$Me$_5$), −8.65 (s, $\nu_{1/2}$ = 80 Hz, 6 H, CH*Me*$_2$), −36.69 (s, $\nu_{1/2}$ = 125 Hz, 1 H); 4, δ 9.44 (d, 1 H, meta), 9.23 (d, 1 H, meta), 8.52 (spt, 1 H, CH*Me*$_2$), 4.73 (spt, 1 H, CH*Me*$_2$), 4.46 (s, 30 H, C$_5$Me$_5$), 2.14 (d, 6 H, CH*Me*$_2$), 1.61 (d, 6 H, CH*Me*$_2$), −1.35 (t, 1 H, para). IR (Nujol mull): 3, 1588 (w), 1434 (vs), 1366 (s), 1342 (w), 1323 (s), 1310 (sh), 1252 (vs), 1197 (vs), 1179 (m), 1158 (vw), 1111 (m), 1097 (m), 1055 (vw), 1042 (w), 1022 (wbr), 936 (w), 886 (s), 862 (vs), 804 (w), 795 (m), 776 (s), 698 (s), 578 (s) cm^{-1}; 4, 1486 (sh), 1468 (vsbr), 1447 (sh), 1424 (s), 1367 (sbr), 1356 (m), 1310 (wbr), 1258 (w), 1238 (vw), 1223 (w), 1211 (m), 1157 (vw), 1107 (w), 1097 (w), 1074 (vw), 1065 (vw), 1052 (w), 1018 (m), 934 (w), 902 (m), 806 (w), 794 (m), 765 (w), 754 (vs), 751 (vs), 667 (vw), 615 (wv) cm^{-1}. Anal. Calcd for 3, $C_{32}H_{47}O_2U$: C, 54.65; H, 6.75. Found: C, 54.77; H, 6.75. Anal. Calcd for 4, $C_{32}H_{47}NOU$: C, 54.93; H, 6.77; N, 2.00. Found: C, 54.89; H, 6.32; N, 1.87.

(9) Crystal data for (a) 3: monoclinic space group $P2_1/c$, a = 9.614(2) Å, b = 17.872(4) Å, c = 17.612(5) Å, β = 97.41(2)°, V = 3000.7(13) Å^3, Z = 4, d_{calcd} = 1.553 g/cm^3. Data were collected at −80 °C utilizing Mo $K\alpha$ radiation (λ = 0.710 73 Å) and 2θ limits of 3–45°. Diffraction data were corrected for absorption, and the structure was solved by direct methods. Hydrogen atoms were placed in idealized positions; [they were not refined. All non-hydrogen atoms were refined anisotropically.] Final residuals were R_F = 0.0285 and R_{wF} = 0.0349 for 2811 reflections with $F_o \geq 3\sigma$. (b) (4): monoclinic space group $P2_1/c$, a = 9.533(3) Å, b = 17.947(4) Å, c = 17.471-(4) Å, β = 96.96(2)°, V = 2967.6(14) Å^3, Z = 4, d_{calcd} = 1.620 g/cm^3. Data were collected at −80 °C utilizing Mo $K\alpha$ radiation (λ = 0.710 73 Å) and 2θ limits of 3–45°. Diffraction data were corrected for absorption, and the structure was solved by direct methods. Hydrogen atoms were placed in idealized positions; [they were not refined. All non-hydrogen atoms were refined anisotropically.] Final residuals were R_F = 0.0247 and R_{wF} = 0.0296 for 3095 reflections with $F_o \geq 3\sigma(F_o)$. Data were collected on a Siemens R3m/v single crystal diffractometer; all calculations were performed utilizing the SHELXTL PLUS software package (Siemens Analytical X-Ray Corporation).
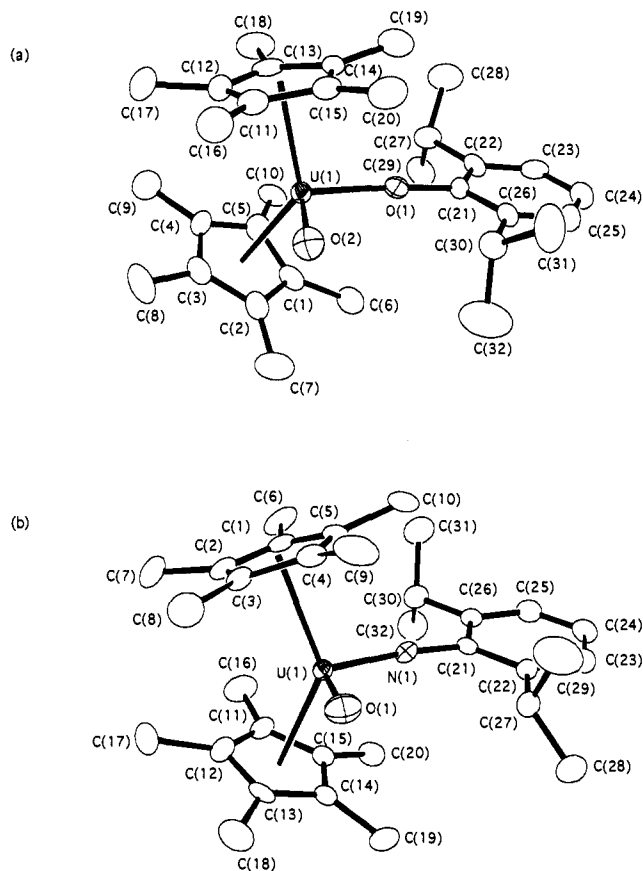
(a)

(b)

Figure 1. ORTEP drawings of (a) $(C_5Me_5)_2U(O-2,6-{}^iPr_2-C_6H_3)(O)$ and (b) $(C_5Me_5)_2U(N-2,6-{}^iPr_2-C_6H_3)(O)$ with atom numbering schemes. Thermal ellipsoids are at 50% probability level. Selected distances (Å) and angles (deg) for **3**: U(1)–O(1) = 2.135(5), U(1)–O(2) = 1.859(6), U(1)–O(1)–C(21) = 169.7(5), O(1)–U(1)–O(2) = 105.9(2). For **4**: U(1)–N(1) = 1.988(4), U(1)–O(1) = 1.844(4), U(1)–N(1)–C(21) = 170.5(4), O(1)–U(1)–N(1) = 110.7(2).

bond length in **3** (U(1)–O(1) = 2.135(5) Å) is slightly longer than those found in structurally characterized U(V) alkoxides (U–O range = 2.03(1)–2.09(2) Å).[11] The uranium–arylimido nitrogen bond length in **4** (U(1)–N(1) = 1.988(4) Å) lies at the high end of the range for structurally characterized U(VI) organoimido compounds (U–N range = 1.854(23)–1.979(8) Å).[3,12] The observed bond lengths as well as the nearly linear U(1)–E(1)–C(21) bond angles (E = O or N) of 169.7(5)° in **3** and 170.5(4)° in **4** may be due to the steric requirements of the 2,6-diisopropylphenyl group. Also of note is the N(1)–U(1)–O(1) bond angle in **4** of 110.7(2)°, which is significantly more obtuse than that of the isoelectronic $(C_5Me_5)_2U(NC_6H_5)_2$ (N(1)–U(1)–N(1') = 98.7(4)°).[3] The origin of this difference, whether electronic or steric, is not yet fully understood. The slight different of the uranium oxo bond distance in these complexes (**3**, U(1)–O(2) = 1.859(6) Å; **4**, U(1)–O(1) = 1.844(4) Å) is consistent with what would be expected from the radii of U(V) and U(VI).[13] These values, however, deviate significantly from a typical uranyl U–O bond length (1.70–1.76 Å)[14] as well as that found in the

α-phase of UOF_4 (1.77(3) and 1.79(2) Å).[15] The longer U–O bond lengths in **3** and **4** may reflect a reduced bond order relative to that suggested for the uranyl ion $(UO_2)^{2+}$.[16]

Steric crowding about the uranium centers is reflected in the solution behavior of these complexes. At room temperature the ${}^1H$ NMR of both monomers indicate rotation about the E–C bonds (**3**, E = O; **4**, E = N) is restricted, giving rise to inequivalent 2,6-diisopropylphenyl resonances.[17] No coalescence for **3** or **4** is observed to 110 °C. Continued heating of these samples results in the slow decomposition (**3**, days; **4**, hours) to unidentified product(s). This solution decomposition also takes place at room temperature over the course of several days. An unusual feature of the ${}^1H$ NMR of **4** is the position of the 2,6-diisopropylphenylimido proton resonances at 9.44, 9.24 (meta), 8.52, 4.73 ($CHMe_2$), and –1.35 (para) ppm, all of which are temperature invariant. We have previously reported similar chemical shifts in other U(VI) phenylimido complexes,[3,12] and the origin of this behavior is currently under investigation. The room-temperature electronic absorption spectra of **3** and **4**, recorded in hexane solution from 1500 to 300 nm, are consistent with the assignments of a U(V) and U(VI) metal center, respectively. The absorption spectrum of **3** shows a single weak transition at 1243 nm (ϵ = 90 M^{-1} cm^{-1}), consistent with an f^1 U(V) metal center.[18] The absorption spectrum of **4** shows no f → f transitions in the near IR, consistent with the assignment of a U(VI) metal center.

In summary, we have extended the synthetic utility of oxidative atom-transfer chemistry to the preparation of the first complexes of uranium(V) and -(VI) containing terminal monooxo functional groups. The structural characterization of these compounds reveals uranium oxo bond lengths longer than those typical for the uranyl ion $(UO_2)^{2+}$, which may reflect a reduced relative bond order. The nature of the bonding of the oxo functional group in **3** and **4** is presently being studied, as is the further utility of this synthetic methodology in preparing organoactinide complexes containing multiply bound functional groups.

Supplementary Material Available: Summary of data collection and refinement, tables of data collection constants, atomic positional parameters, anisotropic thermal parameters, selected bond lengths and angles, and hydrogen atom positions for **3** and **4** (21 pages); observed and calculated structure factors for **3** and **4** (28 pages). Ordering information is given on any current masthead page.

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(15) A neutron diffraction study of α-UOF₄ (ref 15b) revealed axial atom distances of 1.870(16) and 1.884(17) Å. This value is close to the average of a terminal U–F bond in UF₆ (1.99 Å) and a uranyl U–O bond (1.70–1.75 Å). This would be the expected value if the oxygen atom is disordered and equally distributed over the two axial sites. The authors concluded that the terminal U–O bond distance in α-UOF₄ probably fell in the range of 1.70–1.75 Å. (a) Paine, R. T.; Ryan, R. R.; Asprey, L. B. *Inorg. Chem.* **1975**, *14*, 1113. (b) Levy, J. H.; Taylor, J. C.; Wilson, P. W. *J. Inorg. Nucl. Chem.* **1977**, *39*, 1989.

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(17) The observation of only one set of isopropyl resonances in the ${}^1H$ NMR spectra for compounds **1** and **2** may be a result of time averaging on the NMR time scale due to a labile THF ligand. The lability of the THF ligand has been confirmed in the case of homleptic uranium alkoxides; see, for example: Van Der Sluys, W. G.; Burns, C. J.; Huffman, J. C.; Sattelberger, A. P. *J. Am. Chem. Soc.* **1988**, *110*, 5924.

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