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Anhydrous Photochemical Uranyl(VI) Reduction: Unprecedented Retention of Equatorial Coordination Accompanying Reversible Axial Oxo/Alkoxide Exchange

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The dioxo actinyl ions AnO_2^{n+} (An = U, Np, Pu, Am; n = 1, 2) comprise a uniform series that exhibit a linear O═An═O geometry irrespective of the oxidation state (i.e., V−VI) or valence electron count (i.e., f^0-f^5).[1] The rigid stereochemistry has been attributed to strong *covalent* bonding arising from overlap between the oxygen 2p orbitals and the spatially extended actinide 5f/6d manifold, one An═O moiety being *reinforced* by the presence of the other trans oxo donor. This unique "inverse trans influence"[2] distinguishes linear actinyl ions from their bent transition metal counterparts in the highest oxidation states and provides measurably stronger and chemically inert dioxo groups in UO_2^{2+} versus MoO_2^{2+}, the latter possessing relatively labile oxo ligands that participate in oxygen-atom transfer reactions.[3]

Contrasting the facile ligand exchange that occurs within the labile equatorial coordination plane, reports detailing activation of the uranyl(VI) dioxo group are rare and confined primarily to two types of processes, the first involving oxo-atom abstraction in electron-rich uranyl(VI) complexes,[4−6] the second occurring during the reduction of uranyl(VI) to uranium(IV).[7−9] Both of these processes are typically accompanied by a significant alteration of the rest of the uranium coordination sphere.

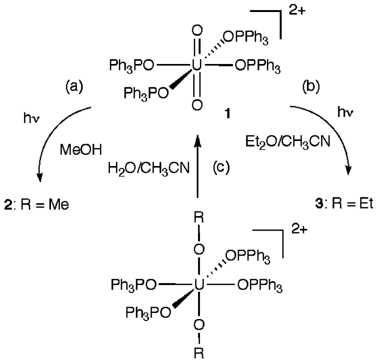
It is in this context that we report herein an unprecedented reversal of this trend. As described below the equatorial coordination sphere is retained following *both* the photochemical reduction of a cationic uranyl(VI) complex with either methanol or diethyl ether *and* subsequent hydrolysis of the uranium(IV) trans alkoxide product, in which the axial sites cleanly and *reversibly* interchange between dioxo and (bis)alkoxide occupancy.

The synthetic protocol entails simply exposing an anhydrous methanol solution of the uranyl(VI) precursor $[UO_2(OPPh_3)_4][OTf]_2$ (**1**)[10] (OTf = O_3SCF_3) to UV light under an inert atmosphere (Scheme 1a). Over a period of 3 h the yellow color of **1** fades and a very pale lavender color gradually appears, from which almost colorless pale green crystals of *trans*-$[U(OMe)_2(OPPh_3)_4][OTf]_2$ (**2**) are obtained.

The generality of this reaction is illustrated by repeating the photolysis of **1** in acetonitrile/diethyl ether, which produces the corresponding uranium(IV) ethoxide derivative *trans*-$[U(OEt)_2(OPPh_3)_4][OTf]_2$ (**3**). In contrast to the short reaction time to form **2**, nearly 24 h are needed for complete conversion of **1** to **3**. Both **2** and **3** are hydrolyzed by adding a few drops of water to an acetonitrile solution, slowly regenerating **1** quantitatively as seen by $^{31}P\{^1H\}$ NMR spectroscopy.

Single crystals of **2** and **3** suitable for X-ray crystallography were obtained from acetonitrile/diethyl ether (Figure 1). The two compounds are nearly isostructural, each revealing crystallographically imposed tetragonal UX_2L_4 symmetry for the uranium center in the solid state, comprising two axial alkoxide groups and four neutral equatorial $OPPh_3$ ligands. Thus apart from the axial site occupancy the solid-state structures of **2** and **3** closely resemble that of the precursor **1**.

Scheme 1. Photochemical Reduction of **1** with (a) Methanol To Form **2**; (b) Diethyl Ether in Acetonitrile To Form **3**; (C) Hydrolysis of **2** or **3** in Acetonitrile To Regenerate **1**



The short U−O(2) bond distance of 2.057(5) Å in **2** is comparable to the terminal U−O bonds found in other structurally characterized uranium methoxide complexes,[11,12] while the linear U−O(2)−C(19) geometry (180.000(1)°) is common for uranium alkoxide complexes and may reflect enhanced π-bonding analogous to that which reinforces the trans uranyl(VI) dioxo geometry. The U−O bond distances (2.330(3) Å) to the $OPPh_3$ ligands are similar to those reported for **1** and within the normal range for uranium(IV) complexes.[13−15]

The X-ray crystallographic data obtained for both **2** and **3** reveal a severely distorted triflate anion. For **3** this disorder precluded anything beyond establishing connectivity, whereas for **2** the program SQUEEZE was applied to allow further structure refinement. The formal U(IV) oxidation state is supported by a combination of isolated versus theoretical yield, elemental analyses, conductivity measurements, electrochemistry, and electronic ab-

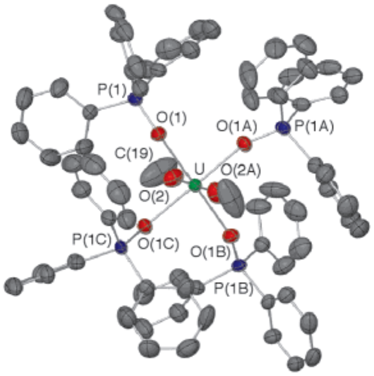


Figure 1. Thermal ellipsoid drawing of the cation of **2**, showing thermal ellipsoids at 50% probability.

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sorption spectroscopy. For example, molar conductivity plots for **1** and **2** are virtually superimposable (Figure S1), indicating that both possess the same 1:2 electrolyte stoichiometry. Cyclic voltammetry conducted on **2** and **3** (Figure S2) reveal quasi-reversible reduction for the U(IV/III) redox couple near −2.4 V with respect to Fc/Fc^+, in accordance with related U(III) examples of the general formula $[UX_2(OPPh_3)_4]^+$ (X = I, OTf),[16,17] while no observable oxidation features are detected, consistent with the absence of known uranium(V) $[UX_2(OPPh_3)_4]^{3+}$ derivatives.

The ^1H and ^{31}P NMR spectra of **2** and **3** in CD_3CN show broad and paramagnetically shifted resonances. A single broad ($\Delta\nu \approx$ 125 Hz) peak is observed at 160 ppm for the chemically equivalent axial methoxy groups in **2**, while the ^{31}P NMR spectrum shows one broad ($\Delta\nu \approx$ 1000 Hz) resonance for the $OPPh_3$ ligands at −88 ppm, substantially upfield relative to free $OPPh_3$ (32 ppm). Similar NMR spectroscopic features are noted for **3**.

The extremely pale colors of compounds **2** and **3** are a consequence of the centrosymmetric geometry and are retained in solution, suggesting that solvent interactions do not substantially disturb the symmetry of the uranium coordination sphere. In methanol or acetonitrile a number of weak bands are present in the visible/NIR region of the absorption spectrum (Figure S3), assignable to Laporte-forbidden f−f transitions consistent with an f^2 electronic configuration that is weakly split by a tetragonal ligand field and spin−orbit coupling.[18,19] Complexes **2** and **3** also display modest solvatochromic properties,[20] the colors appearing faint lavender in methanol and pale green in acetonitrile, which may be ascribed to more effective ion pair separation through H-bonding of the triflate anions in methanol versus acetonitrile.

It has been demonstrated that the photochemical oxidation of primary alcohols by uranyl(VI) is initiated by H-atom abstraction, relying on the strong oxidizing ability of the $^*UO_2^{2+}$ excited state, to generate UO_2^+ and an α-hydroxyl radical (eq 1), which in turn is capable of reducing another equivalent of uranyl(VI) (eq 2).[21] The next step typically involves prompt disproportionation of the unstable UO_2^+ intermediate (equation 3); combining the three reactions eventually leads to complete conversion of uranyl(VI) to uranium(IV).

$$^*UO_2^{\,2+} + RCH_2OH \rightarrow UO_2^{\,+} + R\dot{C}HOH + H^+ \qquad (1)$$

$$UO_2^{\,2+} + R\dot{C}HOH \rightarrow UO_2^{\,+} + RC(O)H + H^+ \qquad (2)$$

$$2\ UO_2^{\,+} + 4\ H^+ \rightarrow UO_2^{\,2+} + U(IV) + 2\ H_2O \qquad (3)$$

However, the observed retention of the equatorial coordination following *both* photolytic reduction of **1** *and* subsequent reoxidation of **2** (or **3**) is at odds with significant ligand scrambling that normally accompanies disproportionation of a labile uranyl(V) intermediate, as typified in the photoreduction of similar uranyl phosphine−oxide complexes.[15] As these related derivatives bear weakly coordinating anionic ligands such as ReO_4^-, the stark contrast in the photochemical reactivity observed here may stem from the *dicationic* charge in **1**, thus encouraging stronger coordination from four bulky neutral phosphine−oxide ligands and in turn providing adequate steric congestion to effectively block the *bimolecular* disproportionation mechanism. This could direct the photochemical process along a different pathway that may involve direct protonolysis of the nucleophilic dioxo group of the uranyl(V) intermediate[22] with retention of stereochemistry. Although unlikely, we cannot exclude the possibility that an overwhelming electronic preference reassembles a trans geometry in high yield following uranyl(V) disproportionation and concomitant ligand scrambling. Future studies will be directed at examining these mechanistic details.

In contrast to the numerous photochemical studies of uranyl(VI) with alcohols the reactivity of ethers has received considerably less attention.[23] It has been postulated that photo-oxidation of diethyl ether proceeds through C−O bond cleavage and H-atom abstraction,[23] thus producing ethanol. In this instance subsequent protonolysis of the dioxo groups furnishes the axial ethoxide ligands in **3** analogous to the photochemical pathway that yields **2**. That ethanol must first be formed photochemically from diethyl ether in order for protonolysis to proceed likely accounts for the much slower reaction time (24 h) to produce **3** compared to **2** (3 h). Indeed, **3** can be accessed directly within hours by irradiating a sample of **1** in dry ethanol.

The results reported here suggest an alternate pathway of dioxo activation that circumvents disproportionation of the putative UO_2^+ intermediate during the anhydrous photochemical reduction of cationic uranyl(VI) complexes with organic substrates. We are continuing our investigations into the photochemical reactivity of related uranyl(VI) systems.

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Supporting Information Available: Synthetic procedures and spectroscopic data for **2** and **3**, Table S1, Figures S1, S2, and S3, and X-ray crystallographic file in CIF format for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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