Contrasting Solvent and Capping Ligand Effects Directing the Photochemistry of Uranyl(VI) Schiff Base Complexes

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The uranyl(VI) ion possesses the rare combination of luminescence and photochemical reactivity. Both properties are attributed to the robust nature of the linear O=U=O group, which gives rise to a long-lived and highly oxidizing $*UO_2^{2+}$ excited state as a result of a uranium 5f ← oxygen 2p LMCT electronic transition.[1] The strong oxidizing ability of the $*UO_2^{2+}$ excited state has been utilized in the catalytic aerobic photooxidation of organic substrates,[2] and applications for uranyl photoreduction have been directed toward improved uranium reprocessing.[3] However, in contrast to the unique excited-state properties of the dioxo group, the photochemistry of uranyl(VI) complexes coordinated by chromophoric ligands that possess their own distinct photochemical properties has not been explored. In our current examination of one such series of N_2O_2 Schiff base ligands, we reveal dramatic solvent and neutral capping ligand (L) effects upon ligand-dominated photochemical processes in complexes of the general formula $UO_2(^tBu_4\text{-salphen})L$ (**1a**: L = THF; **1b**: L = OPMe₃). In one instance these influences combine with an energy-transfer process that redirects the photochemical pathway to the uranyl center and induces a redox transformation involving a capping THF ligand and cobaltocene, the details of which are provided below.

Complexes **1a** and **1b** exhibit quasi-reversible one-electron reduction in THF with NBu_4PF_6 electrolyte at −1.64 and −1.71 V versus Fc^+/Fc, respectively, corresponding to the uranyl(VI/V) redox couple. At these potentials the reducing agent cobaltocene ($E_{1/2}$ = −1.33 V)[4] is unable to induce uranyl(VI) reduction. However, while a stoichiometric mixture of **1a** and cobaltocene in toluene remains unreacted upon exposure to UV light (Scheme 1a), photolysis of the same combination in THF yields the anionic uranyl(VI) hydroxide complex $[Cp_2Co][UO_2(^tBu_4\text{-salphen})(OH)]$ (**2**) as an air-stable bright-orange solid (Scheme 1b) within 2 h. Isolated yields of **2** typically range between 65 and 69%.

Single crystals of **2** suitable for X-ray crystallography were obtained from acetonitrile (Figure 1). The solid-state structure of the anion exhibits a seven-coordinate pentagonal bipyramidal geometry as observed in other structurally characterized uranyl complexes coordinated by salphen Schiff base ligands.[5-7] The trans dioxo group occupies the axial sites while the pentagonal coordination plane comprises the N_2O_2 donor set of the tetradentate Schiff base ligand and the oxygen atom O(5) from the anionic hydroxyl group. Nestled into the cavity provided by the "boat" conformation that tilts the aryloxide rings above the equatorial plane resides the $[Co(C_5H_5)_2]^+$ countercation, which offsets the charge of the uranyl-(VI) anion in **2** resulting from replacement of the neutral donor in **1a** with a hydroxyl group. The Co atom is situated directly above the O=U=O bond axis (approximately 3.8 Å above O(3)) with the $Cp_{(cent)}-Co-Cp_{(cent)}$ axis oriented roughly perpendicular to the plane of symmetry that bisects the uranyl(VI) Schiff base anion.

The structural parameters within the uranyl dioxo unit and between the uranium(VI) center and the various donor atoms of the Schiff base ligands in **2** are all within the normal range, with

Scheme 1. Photolysis of **1a-b** with 1 equiv of Cp₂Co in the Solvent as Listed
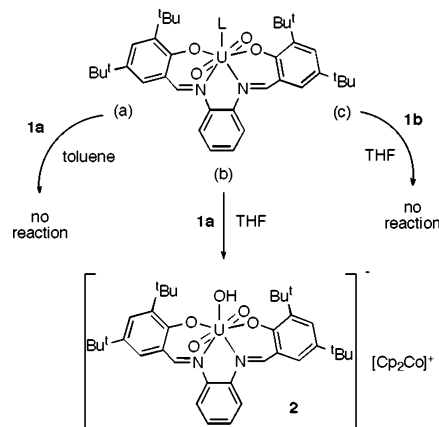
modest elongation of one of the axial U=O bonds (U(1)−O(4) = 1.801(4) Å). Whereas uranyl(VI) hydrolysis commonly yields multinuclear compounds with bridging hydroxyl groups, **2** is a rare example of a uranyl(VI) complex possessing a terminal hydroxyl ligand.[8] The U(1)−O(5) bond distance of 2.240(4) Å is within the range of U−O bond distances (2.229(5)−2.275(5) Å) reported for the terminal hydroxyl ligands in $[Co(NH_3)_6]_2[UO_2(OH)_4]\cdot H_2O$.[8]

The ^1H NMR spectrum obtained for **2** shows equivalent resonances for the two sides of the Schiff base ligand consistent with the approximate C_s point group symmetry observed in the solid-state structure. Additionally, a singlet at 2.36 ppm can be assigned to the hydroxyl proton, and another singlet at 5.66 ppm belongs to the ring protons of the oxidized cobaltocenium ion.

Although adventitious water may seem a logical source of the equatorial hydroxyl ligand in **2**, evidence that this group in fact originates from redox activation of THF comes from (1) the high reproducible isolated yield of **2**, especially for a photochemical reaction, but *only* when the reaction is conducted in THF, (2) the addition of trace water prior to photolysis resulting in decomposi-
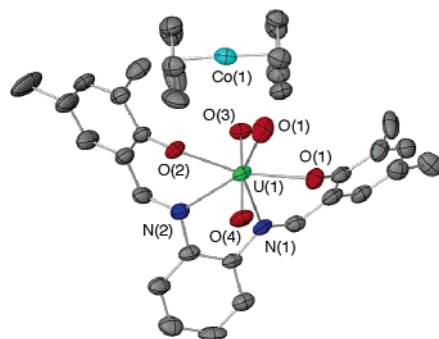

Figure 1. Thermal ellipsoid drawing of **2**, showing thermal ellipsoids at 50% probability. Me groups are omitted for clarity.
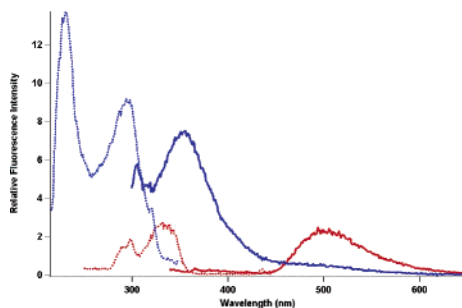
Figure 2. Ambient temperature excitation (dashed line) and emission (solid line) spectra of **1a** (<1.0 μM) in THF (blue; λ_{ex} = 295 nm, λ_{em} = 367 nm) and toluene (red; λ_{ex} = 346 nm, λ_{em} = 510 nm).

tion, and, most convincingly, (3) the fact that in THF-d_8 the reaction is twice as slow, consistent with a primary kinetic isotope effect, and yields a labeled OD group for **2** that is observed at 2.49 ppm in the ^{2}H NMR spectrum.[9]

Insight into these observations can be elucidated from a combination of absorption and fluorescence spectroscopy and varying experimental parameters (i.e., solvent, capping ligand). For example, the electronic excitation and emission spectra for the precursor **1a** shown in Figure 2 reveal distinct differences in the spectral features obtained in toluene versus THF. In toluene there is a significant Stokes' shift (~9100 cm^{-1}) for **1a** that is similarly observed for the free ligand but is absent in the much stronger emission for **1a** in THF. Stokes' shifts and related photochromism[10] in Schiff base compounds have been attributed to cis−trans isomerization of the keto tautomer,[11] thus yielding emission from a structurally altered excited state. It should be noted that the similarities in the emission spectra between **1a** and the free ligand extend to anomalously short ($\tau \sim$ 3 ns) lifetimes when compared to the longer lifetimes normally associated with the *UO$_2$$^{2+}$ excited state.[1] Therefore **1a** represents a rare example of a uranyl(VI) complex displaying luminescence that circumvents the *UO$_2$$^{2+}$ excited state, proceeding instead along a competitive *ligand-based* photochemical pathway.[12]

For **1a** to exhibit spectral features that resemble those observed for the free Schiff base ligand suggests comparable excited-state behavior, whereby structural rearrangement in the uranyl(VI) analogue is initiated with cleavage of the U−O tether to the aryloxide portion of the Schiff base ligand. The ensuing isomerization is significantly facilitated in the noncoordinating solvent toluene through reduced steric interactions upon dissociation of the neutral capping THF ligand.[13] Conversely, rapid solvation in THF retains occupation of the fifth equatorial site and blocks the structural rearrangement. Inhibiting this quenching mechanism permits high-intensity emission from the higher excited state (i.e., with no Stokes' shift), whereupon this emission energy coincides with a U(5f) ← salphen(O) LMCT band[14] centered near 360 nm. This absorption feature is clearly discernible in the electronic absorption spectrum of **1a** and absent in the corresponding spectrum belonging to the free ligand (Figure S1). The ensuing energy transfer to a *metal-centered excited state* is thus responsible for the photochemical reaction that generates **2**. It should be noted that this excited state is higher in energy than the one populated by the U(5f) ← O(2p) LMCT band that is normally associated with uranyl-(VI) photochemistry.

There are two likely pathways for the photochemical reaction to proceed. The first entails initial photooxidation of cobaltocene, but the resulting uranyl(V) species is not expected to be capable of activating THF as indicated by the stable quasi-reversible redox chemistry exhibited by **1a** in THF. Alternatively, intramolecular photochemical activation of coordinated THF could provide both the source of the hydroxyl ligand and subsequent oxidation of Cp$_2$-Co. The photolysis of ethers by uranyl(VI) has been reported,[15] while there is existing literature on a myriad of THF fragmentation and deoxygenation reactions induced by oxophilic metals.[16−18]

Further evidence that intramolecular photoactivation of a coordinated THF molecule leads to the formation of **2** is provided by the O=PMe$_3$ adduct **1b**. It is well established that phosphine oxides form strong metal−ligand bonds with the uranyl(VI) center, which is supported by the quasi-reversible reduction of **1b** in the noncoordinating solvent CH$_2$Cl$_2$, suggesting that ligand dissociation is absent even in the labile uranyl(V) species.[13] Accordingly, irradiation of **1b** with cobaltocene generates no reaction even in THF (Scheme 1c), whereby the capping O=PMe$_3$ ligand prevents THF solvation required for the photochemical reaction that produces **2**.

We are continuing our investigations into the photochemistry of other uranyl(VI) Schiff base complexes.

Supporting Information Available: Synthetic procedures and spectroscopic data for **2**, Table S1, Figure S1, 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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