7620 *Inorg. Chem.* **2010**, *49*, 7620–7622
DOI: 10.1021/ic101136j

Inorganic Chemistry
Communication

Crystallographic Evidence of a Base-Free Uranium(IV) Terminal Oxo Species

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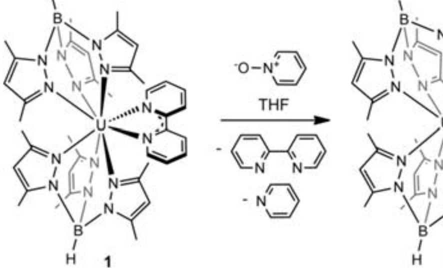
Received June 5, 2010

The uranium(IV) terminal oxo species $Tp^*_2U(O)$ has been synthesized by oxygen-atom transfer from pyridine-*N*-oxide to Tp^*_2U(2,2′-bipyridine), a trivalent uranium species with a monoanionic bipyridine ligand. Full characterization of the oxo species using ^1H NMR and IR spectroscopies, X-ray crystallography, and computational studies was performed.

Redox-active ligands have been demonstrated to effectively support a variety of low-valent transition metals[1] and uranium.[2] These ligands can store electrons from highly reduced metal centers, thus preventing unwanted side reactions such as ligand dissociation and metal precipitation.[1] As these ligands gain popularity, studies are being performed to learn of the types of reactivity these "masked" metal centers are capable of exhibiting.[1−3] Our laboratory has recently reported the synthesis of Tp^*_2U(2,2′-bpy) [**1**; Tp* = hydrotris(3,5-dimethylpyrazolyl)borate; 2,2′-bpy = 2,2′-bipyridine], which contains a trivalent uranium center with a redox-active monoreduced bipyridine ligand.[4] Given the increased recent interest in high-valent uranium oxo species,[5] we set out to determine what role, if any, the redox-active bipyridine plays in stabilizing the electron-rich uranium center during oxygen-atom transfer.

The addition of 1 equiv of pyridine-*N*-oxide to a stirring tetrahydrofuran (THF) solution of the brown-red **1** resulted in an immediate color change to bright pink. Removal of THF *in vacuo* followed by the addition of diethyl ether and filtering allowed isolation of the dark-pink product (**2**) in moderate yields (eq 1).



(1)

Analysis by ^1H NMR spectroscopy revealed a very simple spectrum (see the Supporting Information) containing only four resonances for **2**, indicating that the 2,2′-bpy ligand had been lost in the reaction and that the two remaining hydrotris(3,5-dimethylpyrazolyl)borate ligands were equivalent in the solution. The two resonances for the methyl peaks appeared at −7.53 and +10.81 ppm, while the resonance for the proton on the pyrazolyl rings appeared at 5.13 ppm. The B−H resonance appeared as an extremely broad singlet at −23.19 ppm. IR spectroscopy performed on solid samples of **2** (KBr pellet) displayed absorption bands at 2524 and 2551 cm^{-1} assignable to the B−H bonds in the molecule, suggesting that the hydrotris(pyrazolyl)borate ligands are inequivalent in the solid state.

Cooling a concentrated diethyl ether solution of **2** to −35 °C in a glovebox freezer resulted in the precipitation of large pink rhombohedral crystals. Analysis by X-ray crystallography revealed the formation of the terminal uranium(IV) oxo species $Tp^*_2U(O)$ (**2**) (Figure 1). The bipyridine ligand is no longer present, leaving a seven-coordinate uranium center with a distorted pentagonal-bipyramidal coordination geometry, where N41 and N11 are in the axial positions and the oxo ligand is located in the pentagonal plane along with N21, N31, N51, and N61.

The structural parameters for $Tp^*_2U(O)$ are presented in Table 1. The U−O bond distance in **2** of 1.863(4) Å is the same within error as the distance reported [1.860(3) Å] for Cp'_2U(O)[4-(dimethylamino)pyridine] [$Cp' = \eta^5$-1,2,4-$(Me_3C)_3C_5H_2$], a base-stabilized terminal uranium(IV) oxo reported by Andersen et al.[6] While the base-free counterpart, $Cp'_2U(O)$,

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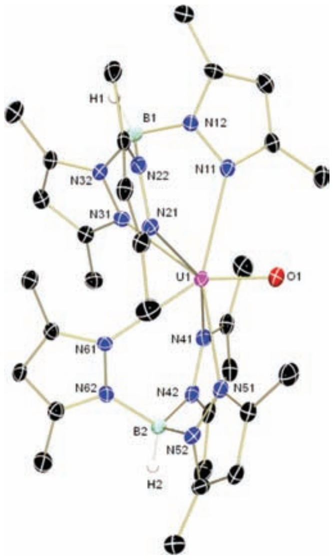

Figure 1. Molecular structure of **2** shown with 30% probability ellipsoids. Solvent molecules and selected hydrogen atoms have been omitted for clarity.

Table 1. Calculated and Experimental Structural Parameters for **2**

bond	length (Å)	calculated
U1−N11	2.541(4)	2.587
U1−N21	2.645(4)	2.695
U1−N31	2.714(4)	2.744
U1−N41	2.532(4)	2.570
U1−N51	2.635(4)	2.674
U1−N61	2.774(4)	2.771
U1−O1	1.863(4)	1.853
	angle (deg)	calculated
O1−U1−N11	105.2(2)	105.79
O1−U1−N21	77.24(16)	77.01
O1−U1−N31	143.69(16)	142.96
O1−U1−N41	101.0(2)	95.66
O1−U1−N51	77.10(16)	76.93
O1−U1−N61	146.11(15)	145.96
N51−U1−N21	154.09(15)	153.53

can be prepared, X-ray-quality crystals were not obtainable.[6] This compound was formed in the same manner, by the addition of pyridine-*N*-oxide to the uranium(III) starting material, Cp′$_2$U(2,2′-bpy). These bond distances are also comparable to the previously synthesized uranium(IV) oxo species Cp*$_2$U(O)[C(NMeCMe)$_2$] (Cp* = η^5-C$_5$Me$_5$), which features stabilization by an N-heterocyclic carbene as the base and a U−O bond distance of 1.916(6) Å.[7] A similar U═O bond distance was calculated by Andrews et al., who reported a bond length of 1.850 Å for U(O) in the gas phase.[8] The U−O bond distances in all of these examples demonstrate the similarity of the structures despite the differences in the ligands and the presence of a coordinated base.

Each hydrotris(pyrazolyl)borate ligand in **2** has one very long U−N bond and two shorter ones. The long distances are 2.714(4) and 2.774(4) Å, while the shorter ones range from 2.541(4) to 2.645(4) Å. The variation in bond distances within a single ligand is typical for uranium compounds with two hydrotris(3,5-dimethylpyrazolyl)borate ligands[9] and is most likely due to a crowded steric environment at the uranium center. The uranium(III) starting material, Tp*$_2$U(2,2′-bipy), also exhibits this behavior. Further characterization by IR spectroscopy was attempted to determine the absorption of the U−O bond. However, the expected region (750−770 cm^{-1})[6] was obscured by peaks from the ligand, as determined by comparison with Tp*$_2$U(2,2′-bipy).

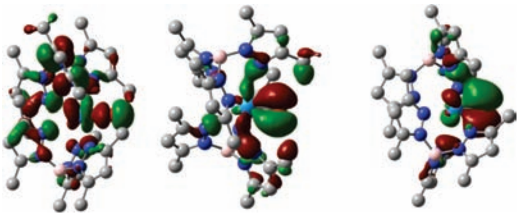

Figure 2. σ, HOMO-13 (left), and two π, HOMO-15 (middle) and HOMO-16 (right), interactions between the uranium and oxygen.

A density functional theory (DFT) analysis was performed on the uranium oxo complex to examine the electronic and molecular structures of **2**. The bond lengths and angles for the optimized structure compare well with the experimentally determined values (Table 1), indicating a good model for **2**. The uranium center has a σ interaction with the oxo ligand, which occurs between the U 5f$_{z^3}$ and O 2p$_z$ orbitals (Figure 2). Additionally, two π interactions are visible, one involving a U 5f orbital and the other a U 6d orbital consistent with a triple bond. The calculated atomic spin density on uranium of 2.13 is anticipated for a 5f^2 system with two unpaired electrons.

The uranium(IV) oxo species reported here, Tp*$_2$U(O), is unstable.[10] Stirring this compound at room temperature for less than 1 h in diethyl ether results in a color change to yellow, producing a complicated ^{1}H NMR spectrum consistent with decomposition. The [HB(3,5-dimethylpyrazole)$_2$]$_2$ dimer could be isolated from the reaction mixture, confirmed by matching unit cells as determined by X-ray crystallography.[11] In addition, analysis by IR spectroscopy showed an absorption at 901 cm^{-1}, indicative of the formation of a *trans*-dioxo unit in uranyl species. The rapid decomposition of **2** is attributed to its base-free nature.

In summary, our laboratory has synthesized a base-free uranium(IV) terminal oxo species by utilizing a redox-active bipyridine fragment. This molecule has been characterized experimentally by ^{1}H NMR and IR spectroscopies as well as X-ray crystallography. The U═O bond distance observed is similar to other crystallographically characterized uranium(IV) oxo species. Analysis by DFT was used to determine the electronic structure and bonding interactions in the complex. Formation of the oxo by the addition of pyridine-*N*-oxide to **1** with a loss of the neutral 2,2′-bpy ligand indicates that this chelator played a key role in supporting the low-valent uranium center prior to O-atom transfer. Thus, it appears that **1** is a convenient entry into bis[hydrotris(3,5-dimethylpyrazolyl)borate] uranium species because a loss of the redox-active bipyridine produces base-free

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functionalities on uranium. Future studies will focus on the formation of new oxygen-element bonds with the oxo fragment.

Acknowledgment. The authors acknowledge financial support from Purdue University and the National Science Foundation (Grant CHE-0541587 and CHE-0910552 to Texas A&M University).

Supporting Information Available: Synthetic procedures and crystallographic and computational details. This material is available free of charge via the Internet at http://pubs.acs.org.