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Exchange of an Imido Ligand in Bis(imido) Complexes of Uranium

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The study of the uranyl ion, UO_2^{2+}, has been central to understanding metal−ligand bonding in the f elements and in determining the extent to which the f electrons participate in such interactions.[1] Our recent isolation of the imido analogues of uranyl, namely, $U(NR)_2^{2+}$, provides another model that can be used to refine our understanding of these phenomena.[2,3] We now report the synthesis of a uranium oxo imido complex, *trans*-$[U(NR)(O)]^{2+}$, which provides a link between the uranyl and bis(imido) extremes.

We have been studying the reactivity of the $[U(NR)_2]^{2+}$ fragment with various Lewis bases, including monodentate amines. For instance, addition of excess aniline to a toluene solution of $U(N^tBu)_2I_2(THF)_2$ quickly results in the deposition of the expected $U(N^tBu)_2I_2(NH_2Ph)_2$ (**1**) as pale-orange plates, in moderate yield (Scheme 1).[4]

However, during one reaction performed in THF, a few small orange blocks were isolated upon recrystallization from toluene. These crystals were quite different in morphology than those of **1**. The material was analyzed by X-ray crystallography and found to be $U(N^tBu)(O)I_2(THF)(NH_2Ph)_2$ (**2**), and its solid-state molecular structure is shown in Figure 1. Complex **2** arises from the partial hydrolysis of the starting bis(imido) complex by trace quantities of water in the solvent or on the glassware (Scheme 1). It possesses a pentagonal bipyramidal geometry similar to those found in many uranyl and uranium bis(imido) complexes. However, its most salient structural features are the oxo and imido ligands, which adopt a *trans* orientation (O1−U1−N1 = 178.6(2)°). The U−O bond length is 1.781(4) Å, comparable to the U−O bond lengths found in the uranyl ion, while the U−N(imido) bond length (1.823(4) Å) is comparable to the U−N bond lengths in the previously characterized uranium *trans*-bis(imido) complexes.

Only one other oxo imido complex has been structurally characterized for uranium, $Cp^*_2U(O)(N\text{-}2,6\text{-}(^iPr)_2C_6H_3)$. In this instance, the oxo and imido ligands are in a *cis* configuration, and the U−N and U−O bond lengths are 1.988(4) and 1.844(4) Å, respectively.[5,6] The structures of *trans*-$[U(O)(NE)Cl_4]^-$ (E = SR_2, PPh_3) are also known. In these complexes, the U−O bond lengths are comparable to those in **2**, but the U−N bond lengths are considerably longer (E = SR_2, U−N = 1.920(3) Å; E = PPh_3, U−N = 1.912(3) Å).[7,8]

We have endeavored to develop a rational synthesis of **2** by direct addition of water; however, addition of 1 equiv of H_2O to $U(N^tBu)_2I_2(THF)_2$ in mixtures of aniline/THF, or neat THF, only provide the products of complete hydrolysis (e.g., $^tBuNH_3I$) or sometimes $UO_2I_2(THF)_3$.[9] Clearly, H_2O is too indiscriminate a reagent to be useful in this instance, and it is likely that only extremely low concentrations of water will lead to hydrolysis of only one imido ligand. In contrast, Chivers and co-workers found that $B(C_6F_5)_3{\cdot}H_2O$ was an effective reagent for selectively exchanging an imido ligand for an oxo group in tellurium imido complexes, without unwanted reactivity.[10]

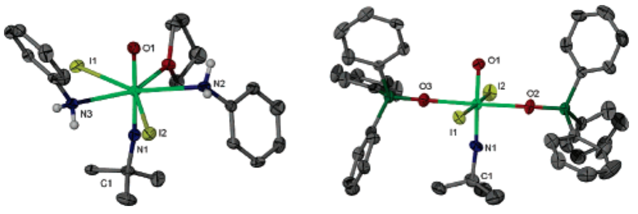
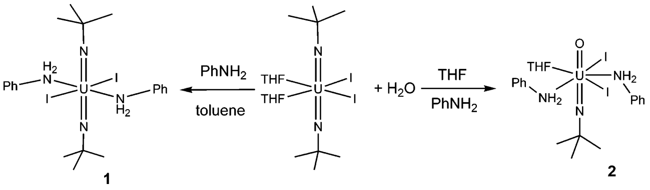
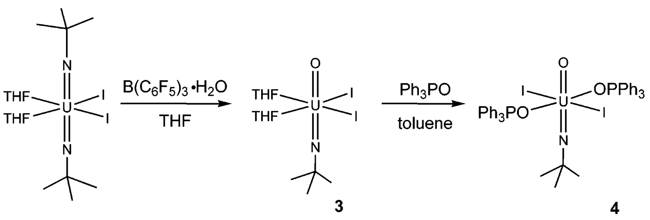


Figure 1. Solid-state molecular structures of $U(N^tBu)(O)I_2(THF)(NH_2Ph)_2$ (**2**) and $U(N^tBu)(O)I_2(Ph_3PO)_2$ (**4**). Selected bond lengths (Å) and angles (deg) for **2**: U1−O1 = 1.781(4), U1−N1 = 1.823(4), U1−O2 = 2.452(4), U1−N2 = 2.632(4), U1−N3 = 2.597(5), U1−I1 = 3.1455(5), U1−I2 = 3.1749(5), O1−U1−N1 = 178.6(2), C1−N1−U1 = 170.4(4). Selected bond lengths (Å) and angles (deg) for **4**: U1−O1 = 1.764(5), U1−N1 = 1.821(7), U1−O2 = 2.335(5), U1−O3 = 2.302(5), U1−I1 = 3.0660(7), U1−I2 = 3.0443(8), O1−U1−N1 = 178.4(3), C1−N1−U1 = 172.3(7).

Scheme 1



Scheme 2



Monitoring an equimolar solution of $B(C_6F_5)_3{\cdot}H_2O$ and $U(N^tBu)_2I_2(THF)_2$ in THF-d_8 by ^1H NMR spectroscopy reveals the growth of two new ^tBu peaks at 0.69 and 1.23 ppm with equal intensity, consistent with the formation of a new uranium imido complex and $B(C_6F_5)_3{\cdot}H_2N^tBu$, respectively. The ^{11}B NMR spectrum of the reaction mixture reveals that a new resonance at −11.1 ppm, assignable to $B(C_6F_5)_3{\cdot}H_2N^tBu$, also appears over the course of the reaction.[10]

On a preparative scale, the reaction of $B(C_6F_5)_3{\cdot}H_2O$ and $U(N^tBu)_2I_2(THF)_2$ in benzene results in the deposition of a red−orange powder within several hours. Crystallization of this powder from THF/hexanes provides $U(N^tBu)(O)I_2(THF)_2$ (**3**) in moderate yields (Scheme 2).

Complex **3** dissolves in benzene and CH_2Cl_2 but quickly precipitates in either solvent to provide a fine orange powder. We attribute this behavior to the loss of a THF ligand and the deposition of insoluble $[U(N^tBu)(O)I_2(THF)]_x$.[11] Not surprisingly, complex **3**

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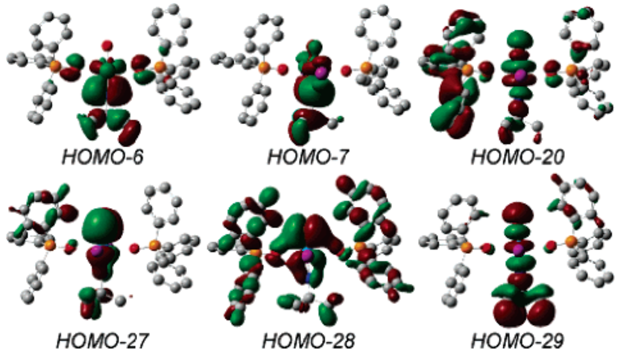

Figure 2. Molecular orbitals of **4** involved in the U═N and U═O bonds. The figure shows four π bonds and two σ bonds. The π bonds are given mostly by interaction between the U d_π and f_π and the 2p orbitals of the N and O. In the σ bonds, the U f_σ and d_σ take part.

is readily soluble in THF or mixtures of CH_2Cl_2 and THF. Complex **3** can be conveniently converted to U(N^{t}Bu)(O)I$_2$(Ph$_3$PO)$_2$ (**4**) by addition of 2 equiv of Ph$_3$PO in toluene (Scheme 2). Like **3**, complex **4** is an orange crystalline solid, which is readily soluble in aromatic solvents and THF. Consistent with the proposed formulation, **4** exhibits a single peak in its ^{31}P NMR spectrum at 47.3 ppm.

Crystals of **3** proved to be badly disordered, but **4** was found to crystallize in the triclinic space group $P\bar{1}$ with two independent molecules in the unit cell. An ORTEP diagram of one of those molecules is shown in Figure 1. The metrical parameters of the oxo imido core (U1−O1 = 1.764(5) Å, U1−N1 = 1.821(7) Å, O1−U1−N1 = 178.4(3)°) are similar to those of **2**, while its U−I and U−O(phosphine oxide) bond lengths are similar to those of the bis(imido) analogue, U(N^{t}Bu)$_2$I$_2$(Ph$_3$PO)$_2$.[3]

Complexes **2** and **4** were studied using hybrid density functional theory,[12] and the optimized structures agree well with the crystallographic data. For example, the calculated structure of **4** exhibits U−N and U−O(uranyl) bond lengths of 1.818 and 1.781 Å, respectively, and a N−U−O(uranyl) angle of 179.5°. The six molecular orbitals involved in the U═N and U═O bonds of **4** are shown in Figure 2.

Like uranyl and the bis(imido) complexes, a total of four π bonds and two σ bonds were identified, giving each ligand a bond order of 3. The participation of the uranium f orbitals in the MOs (in order of descending energy) is 15, 19, 32, 7, 3, and 0%, while the participation of the d orbitals (in the same order) is 8, 10, 7, 13, 9, and 7%. The uranium 6p orbital was found to participate in one σ bond (HOMO-20) with a contribution of 6.5%. Interestingly, the two π bonding orbitals involved in the U−O bond have a larger component of d character, while in the U−N bond the uranium f orbitals plays a larger role. Contrary to the bis(imido) complexes, the different nature of the two ligands (O vs N^{t}Bu) breaks the symmetry of the orbitals. The bonding orbitals are, therefore, more clearly defined as belonging to the U−N (HOMO-6, -7, -29) or the U−O (HOMO-20, -27, -28) bonds. The total Mulliken and NBO calculated positive charges on the metal center are 1.60 and 1.45, respectively, compared to 1.50 and 1.27, respectively, for the bis(imido) system.[3] The greater charge at the metal center suggests that the M−L multiple bonding in **2** and **4** is less covalent than in the bis(imido) analogues.

A vibrational mode analysis of complex **4** identified a U−O mode at 903 cm^{-1}, whereas the U−N mode couples with the N−C mode, leading to three bands at 1142, 1144, and 1159 cm^{-1}. The simulation has helped us identify the U−O and U−N vibrations in the IR spectrum of complex **4**. As a KBr pellet, the IR spectrum of **4** exhibits a band at 858 cm^{-1}, which we attribute to the U−O vibration, and bands at 1128 and 1134 cm^{-1}, which we attribute to the U−N vibrations. For complex **3**, we have unambiguously identified the U−O vibration at 883 cm^{-1} (KBr pellet), as this peak is shifted to 827 cm^{-1} in the IR spectrum of **3**-^{18}O.[13] For comparison, the U−O vibration in Cp*U(O)(N-2,4,6-Me$_3$C$_6$H$_2$) was observed at 775 cm^{-1}.[6]

In conclusion, the synthesis of **4** provides a bridge between the isostructural uranyl analogue, UO$_2$I$_2$(Ph$_3$PO)$_2$,[14] and the bis(imido) congener, U(N^{t}Bu)$_2$I$_2$(Ph$_3$PO)$_2$. The use of the borane adduct of water to exchange oxo for imido suggests that similar synthetic strategies using borane adducts of amines may be a viable route to mixed bis(imido) complexes. The structural data and theoretical results for **2** and **4** demonstrate that, like the bis(imido) complexes, the mixed oxo imido species still maintain many of the qualities that uranyl possesses, including significant uranium f and d electron participation in the multiple bonds.

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Supporting Information Available: Complete details of the preparation and characterization of **1**−**4**, including X-ray crystallographic details (as CIF files) of **1**, **2**, and **4**. Geometries of the calculated structures of complexes **2** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) Complete details of the theoretical calculations can be found in the Supporting Information.
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