

## Extending the Chemistry of the Uranyl Ion: Lewis Acid Coordination to a U=O Oxygen

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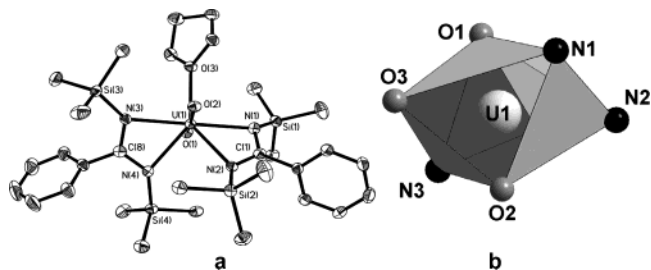
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The chemistry of uranium has been dominated by the uranyl dication  $[\text{UO}_2]^{2+}$  because of the largely inert nature of the  $\text{U}=\text{O}$  bonds.<sup>1,2</sup> The trans arrangement of the oxo ligands, a well-established feature of the actinyls, originates from the combination of metal 5f/6d and oxygen 2p orbitals to form stable  $\text{U}=\text{O}$  bonds.<sup>3</sup> However it is becoming apparent that, under certain conditions, the oxo ligands can undergo ligand exchange,<sup>4</sup> scrambling<sup>5,6</sup> and substitution reactions.<sup>7,8</sup> We believe that, in most cases, the origin of this reactivity lies in the Lewis basic nature of the  $\text{U}=\text{O}$  oxygens. Although the formal charge on the uranium is 2+, experimental<sup>9</sup> and theoretical<sup>10</sup> evidence suggests the effective nuclear charge is closer to 3+, depending on equatorial ligand overlap.<sup>3</sup> The extent to which the equatorial ligands quench the charge at uranium determines the amount of electron density drawn from the axial oxygens. As such, each of the oxygens can bear a slight negative charge, rendering the oxo ligands Lewis basic. In this respect, uranyl oxygens are known to interact with cations in inorganic uranate compounds,<sup>11–13</sup> and there is an increasing number of discrete molecules containing  $\text{U}=\text{O}-\text{M}$  structural motifs ( $\text{M} = \text{Li}, \text{Na}, \text{NH}_4$ ).<sup>4,14,15</sup> We believed that, through tailoring the coordination environment in the equatorial plane, we could further enhance the Lewis basic properties and promote direct coordination to a Lewis acid for the first time. To this end we have synthesized a novel benzaminato complex that can bond to the strong Lewis acid  $\text{B}(\text{C}_6\text{F}_5)_3$  through one uranyl oxygen.

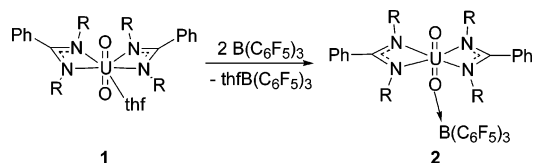
The precursor  $\text{UO}_2(\text{NCN})_2\text{thf}$  (**1**) [ $\text{NCN} = \{(\text{SiMe}_3)_3\text{CPh}(\text{NSiMe}_3)\}$ ] is synthesized by the metathesis reaction of 2  $\text{Na}[\text{NCN}]$  with  $\text{UO}_2\text{Cl}_2(\text{thf})_3$ .<sup>16,17</sup> The structure of complex **1** (Figure 1a) is unusual because the NCN ligands are distorted from the equatorial plane to such an extent that the geometry can no longer be described as bipyramidal, the prototypical geometry in uranyl chemistry (Figure 1b). The uranium center is seven-coordinate, with a thf molecule and two bidentate benzaminato ligands that are twisted out of the equatorial plane (the plane normal to the vector defined by O1 and O2) by 23.8 and 24.5°, corresponding to ligand atom equatorial displacement of up to 0.62 Å. The uranyl unit is significantly bent toward the thf ligand ( $\text{O1}-\text{U1}-\text{O2}$  169.7(2)°), and two of the nitrogen ligand atoms are essentially trans to each other ( $\text{N1}-\text{U1}-\text{N3}$  177.09(16)°). The atoms O1, O2, N1, N3 are near coplanar and can best be visualized as forming the quadrilateral face of a trigonal prism that is capped by the thf oxygen atom (O3) (Figure 1b).

The  $\nu_1$   $\text{O}=\text{U}=\text{O}$  stretch for **1** (803  $\text{cm}^{-1}$ ) indicates a weakening of the  $\text{U}=\text{O}$  bonds (cf.  $[\text{UO}_2\text{Cl}_2(\text{thf})_2]$ ,  $\nu_1$  840  $\text{cm}^{-1}$ ) and an increase in Lewis basicity. By adding 2 equiv of  $\text{B}(\text{C}_6\text{F}_5)_3$  to **1** the expected removal of coordinated thf and formation of a  $\text{U}=\text{O}-\text{B}$  bond takes place, giving an immediate color change from orange to deep



**Figure 1.** (a) Molecular structure for  $[\text{UO}_2(\text{NCN})_2(\text{thf})]$  (**1**) (50% ellipsoids); (b) polyhedral representation showing only the atoms coordinated directly to uranium for clarity (N4 obscured).

**Scheme 1.** Coordination of  $\text{B}(\text{C}_6\text{F}_5)_3$  to a  $\text{U}=\text{O}$  Bond ( $\text{R} = \text{SiMe}_3$ )



magenta. Multinuclear NMR spectroscopy ( $^1\text{H}$ ,  $^{19}\text{F}$ ,  $^{11}\text{B}$ , and  $^{13}\text{C}$ ) indicates the formation of  $\text{UO}\{\text{OB}(\text{C}_6\text{F}_5)_3\}(\text{NCN})_2$  **2** (Scheme 1).

Crystals of **2** suitable for X-ray diffraction were grown from a hexane/benzene solution and confirm this assignment (Figure 2).

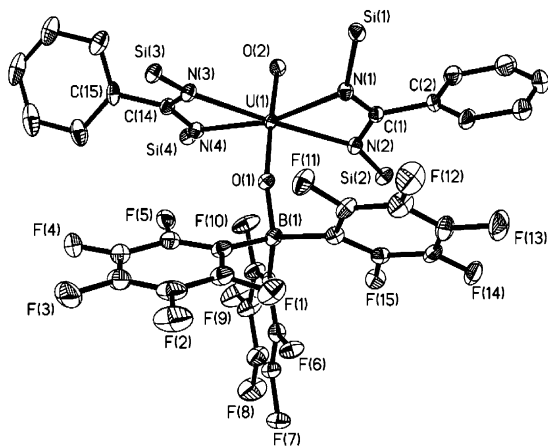
The borane coordinates directly to one oxo ligand with a  $\text{B}-\text{O}$  bond length ( $\text{B1}-\text{O1}$ , 1.545(6) Å) in the range of those observed for d-block metal oxo-borane adducts ( $\text{B}-\text{O}$ , 1.460(6)–1.568(5) Å).<sup>18</sup> The uranyl unit remains essentially linear ( $\text{O1}-\text{U1}-\text{O2}$ , 177.45(14)°), but the coordinated oxo ligand has an elongated  $\text{U}=\text{O}$  bond ( $\text{U1}-\text{O1}$ , 1.898(3) Å) compared to the uncoordinated one ( $\text{U1}-\text{O2}$ , 1.770(3) Å); the latter being typical for uranyl complexes.<sup>2</sup> The  $\text{U}=\text{O}-\text{B}$  interaction appears stronger than alkali metal interactions  $\text{U}=\text{O}-\text{M}$  ( $\text{M} = \text{Li}, \text{Na}$ ) judging by the changes observed in  $\text{U}=\text{O}$  bond lengths. For example, the amido complexes  $[\text{thf}_2\text{Na}][\text{UO}_2(\text{NCN})_3]$  ( $\text{U}=\text{O}$ , 1.812(3), 1.783(3) Å)<sup>17</sup> and  $[\text{thf}_2\text{Na}][\text{UO}_2\{\text{N}(\text{SiMe}_3)_2\}_3]$  ( $\text{U}=\text{O}$ , 1.810(5), 1.781(5) Å)<sup>19</sup> contain one short and one elongated  $\text{U}=\text{O}$  bond, but this elongation is significantly less than that in **2** ( $\text{U1}-\text{O1}$ , 1.898(3) Å).

Coordination to the boron displaces electron density away from the  $\text{U}=\text{O}$  bond and causes a number of things to happen. First, the  $\text{U}=\text{O}$  bond strength in **2** decreases, leading to a reduced  $\text{O}=\text{U}=\text{O}$  symmetric stretching frequency ( $\nu_1$ , Raman = 780  $\text{cm}^{-1}$ ), compared to **1** (803  $\text{cm}^{-1}$ ), and is to our knowledge the lowest reported for a mononuclear uranyl(VI) complex.<sup>6</sup> This unusual coordination is maintained in solution with Raman ( $\text{C}_6\text{D}_6$ ) ( $\nu_1$ , 778  $\text{cm}^{-1}$ ) and  $^{11}\text{B}$  NMR chemical shift (−10.6 ppm, cf. 60 ppm for  $\text{B}(\text{C}_6\text{F}_5)_3$ ), indicating that the  $\text{U}=\text{O}-\text{B}$  bond remains intact.

Secondly, this removal of charge also results in an increased interaction between uranium and the equatorial ligands, evident in

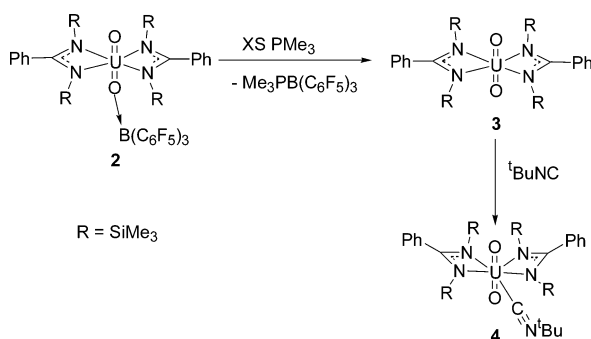
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**Figure 2.** ORTEP diagram of **2** at the 50% ellipsoid level. The methyl groups on the Si atoms are omitted for clarity.

### Scheme 2



the decrease in U–N bond length from **1** (U–N(av), 2.463(4) Å) to **2** (U–N(av), 2.371(4) Å). The change in electron distribution throughout the molecule is also reflected in the electronic absorption spectrum. Most uranyl compounds are yellow/orange and exhibit a weak absorption band with vibronic fine structure between 420 and 450 nm due to forbidden O-to-U LMCT bands. Toluene solutions of complex **2** show a number of intense electronic absorptions including a broad unstructured band at  $\lambda_{\max} = 600$  nm that tails off at 710 nm, hence the deep magenta color of **2**.

Finally, the removal of the thf molecule in **1** reduces the steric interactions around the metal center, and the NCN ligands “relax” back into the equatorial plane of **2**.

To explore the chemistry of the coordinatively unsaturated uranium center in **2**, the strong Lewis base  $\text{PMe}_3$  (2 equiv), known to form the  $\text{Me}_3\text{PB}(\text{C}_6\text{F}_5)_3$  adduct (insoluble in hydrocarbon solvents), was used.<sup>20</sup> On addition of  $\text{PMe}_3$  to solutions of **2** ( $\text{C}_6\text{D}_6$ ) there is an immediate color change from magenta to orange/yellow with the precipitation of  $\text{Me}_3\text{PB}(\text{C}_6\text{F}_5)_3$  (Scheme 2).  $^1\text{H}$  and  $^{13}\text{C}$  NMR confirmed clean conversion of **2** to **3** with a downfield shift for each of the *o*-Ph and  $\text{SiMe}_3$  signals. The O=U=O symmetric stretching frequency ( $\nu_1$ , 818  $\text{cm}^{-1}$ ) increases from **2** to **3** as the metal center establishes stronger U=O bonds. Despite the fact that **3** is coordinatively unsaturated compared to **1**,  $\text{PMe}_3$  does not bond to the uranium center, although the same reaction with thf reproduces **1** quantitatively by NMR spectroscopy reflecting the “hardness” of the metal center.

The utility of complex **3** is illustrated in the formation of the first uranyl complex containing a coordinated isonitrile ligand. Treatment of a toluene solution of **3** with 1 equiv of *tert*-butylisonitrile ( $^t\text{BuNC}$ ) cleanly forms  $[\text{UO}_2(\text{CN}^t\text{Bu})(\text{NCN})_2]$  (**4**) (Scheme

2). Compound **4** can be made directly from **2** by the addition of 2 equiv of  $^t\text{BuNC}$ .<sup>21</sup> Solid samples of **4** can be isolated, and  $^1\text{H}$  and  $^{13}\text{C}$  NMR and Raman spectroscopy confirm coordination of the isonitrile ligand. The Raman spectrum of **4** shows a characteristic C≡N stretch at 2192  $\text{cm}^{-1}$ , increased from that of free  $^t\text{BuNC}$  (C≡N, 2040  $\text{cm}^{-1}$ ) as observed in other complexes containing purely N≡C–M  $\sigma$ -bonds.<sup>22</sup> Also, the change in chemical shift from free ligand (N≡C, 153.7 ppm) to coordinated ligand in **4** (N≡C, 126.6 ppm) is typical of the reduction in antibonding contribution to C≡N bonding.<sup>22</sup> The difference in  $\nu_1$ , 816  $\text{cm}^{-1}$  compared to **1** ( $\nu_1$ , 803  $\text{cm}^{-1}$ ) suggests that, in these systems,  $^t\text{BuNC}$  is a poor ligand compared to thf. Complex **4** is the third report of a complex exhibiting a uranyl–carbon interaction.<sup>23,24</sup>

In conclusion, careful selection of ligands (NCN) can lead to the formation of a uranyl complex that does not exhibit classical equatorial coordination (**1**). The increased Lewis basicity of **1** is exploited by coordinating to a strong Lewis acid, providing a new structural motif for the uranyl ion (**2**). Fundamental changes to the bonding in the uranyl can be probed by vibrational and electronic spectroscopy.<sup>3</sup> Removal of the Lewis acid affords a coordinatively unsaturated complex (**3**) that can incorporate novel ligands, e.g.,  $^t\text{BuNC}$  (**4**). We are currently exploring the chemistry of **2** in the expectation of increased reactivity of the U=O bonds.

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**Supporting Information Available:** X-ray crystallographic files of **1** and **2** (CIF) and Raman spectra of **1–4** and UV/vis spectra of **2** and **3** along with experimental details describing the synthesis of **1–4** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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