Synthesis of Imido Analogs of the Uranyl Ion

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Here we describe the synthesis of two imido analogs of the uranyl ion, UO$_2$$^{2+}$, in which the oxygenes are replaced by divalent alkyl or aryl nitrogen groups: U(N' Bu)$_2$J$_2$(THF)$_2$ (1) and U(NPh)$_2$J$_2$(THF)$_3$ (2) (where N' Bu is tert-buty1 and THF is tetrahydrofuran). Both compounds have been fully characterized by standard analytical techniques, including x-ray crystallography, and the chemical bonding between the metal center and the nitrogen ligands was quantified by using hybrid density functional theory calculations. As expected for a uranyl analog, these complexes exhibit linear N-U-N linkages and very short U-N bonds. In addition, the theoretical calculations show strong involvement of the 5f and 6d electrons in the U-N bonding.

The uranyl (UO$_2$$^{2+}$) species is the most common functional unit in the chemistry of U(VI) and has been known for more than 150 years (1). With the advent of nuclear energy and the use of uranium oxide as reactor fuel, the chemistry of the uranyl ion has played an essential role in the processing of uranium ore, nuclear fuel, and waste (2). The linear arrangement of the oxo ligands, extremely short U-O bond lengths, and high thermal and chemical stability reflect some of the unusual properties of this functional group (3). Given the prevalence of uranyl, it is surprising that metal-ligand multiple bonding in the actinides is not better understood. For instance, it is generally agreed that the uranium-oxygen bonds in uranyl involve six U-O interactions; however, the ordering of the frontier orbitals is still being debated (4). Furthermore, recent high-profile reports, such as the synthesis of a molecular uranium nitride (5) and the isolation of an η$^1$-O-bound uranium-CO$_2$ complex (6), point to a general deficiency in our knowledge of the chemistry of the f elements relative to the transition metals. The importance of multiple bonding in the actinides and the extent that the f orbitals participate in bonding are still open questions that can be addressed through the synthesis of new classes of compounds.

The imido ligand (NR$^2$–) is isoelectronic with the oxo ligand, and the two groups can often be interchanged in transition metal complexes. The alkyl or aryl substituent of the imido ligand provides a variable unavailable in oxo chemistry, because changes in the steric and electronic properties of the imido substituent can affect the chemical of the metal center to which it is bound. The synthesis of the isoelectronic imido analogs of uranyl has therefore been of interest for many years (7). However, direct imido analogs of the uranyl ion have remained elusive despite a great deal of effort toward their synthesis. For instance, Denning and co-workers were able to isolate the phosphorane-iminato (UNPR$_3$) and sulfilimine (UNSR$_3$) substituted analogs of uranyl, which are heteroatom approximations to the imido ligand (7–9). Burns and co-workers were able to synthesize C$_p^*$$_2$U(NR)$_2$ (where R was either Ph or adamantyl and C$_p^*$ was C$_5$Me$_5$), but with imido groups in a cis configuration (10, 11). The difficulty in isolating a trans-bis(alkyl or aryl imido) complex led Denning to speculate that their isolation was not possible because uranium(VI) is too oxidizing (9).

Here we report the synthesis and full characterization of both alkyl and aryl trans-bis(imido) analogs of the uranyl ion: U(NR)$_2$$^{2+}$. By using hybrid density functional theory (DFT), we also compare the calculated and experimental properties of these compounds and analyze the nature of the U-N bonding (12–15).

Reaction of uranium turnings with 3 equivalents of I$_2$ and 6 equivalents of tert-buty1amine in tetrahydrofuran (THF) quickly results in metal dissolution and the formation of an orange solution (Scheme 1). Isolation of a crude orange solid and recrystallization from a toluene/hexanes solution provides crystalline U(N' Bu)$_2$I$_2$(THF)$_2$ (1) in 68% yield (16).

Replacing tert-buty1amine with aniline in Scheme 1 does not provide any tractable products. However, by starting with well-known...


UI₃(THF)₃ (17) instead of uranium metal, a bis(imido) complex could be made in 84% yield. Thus, addition of 1.5 equivalents of I² to a THF solution of UI₃(THF)₆ aniline (2 equivalents), and NEt₃ (4 equivalents) generates orange-brown solutions containing U(NPh)₂I₂(THF)₃ (2) (Scheme 2) (18).

Complex 1 is an orange, moisture-sensitive, crystalline solid, which is soluble in THF and toluene. The ¹H nuclear magnetic resonance (NMR) spectrum of 1 displays resonances for both THF ligands and tert-butyl groups in a 1:1 ratio. One THF resonance occurs at 4.56 parts per million (ppm), whereas the other occurs at 1.54 ppm. Complex 2 is a red-brown crystalline solid with similar solubility properties to 1. Its ¹H NMR spectrum exhibits resonances for three equivalent THF ligands and two equivalent phenyl moieties. Its two THF resonances are observed at 4.38 ppm and 1.41 ppm. Addition of excess THF to NMR samples of 1 or 2 causes these resonances to shift to the values anticipated for free THF, suggesting rapid exchange of coordinated and uncoordinated THF molecules on the NMR time scale.

The infrared (IR) spectra of complexes 1 and 2 show strong vibrations at 1170 cm⁻¹ and 1270 cm⁻¹, respectively, which is in the region expected for a trans imido complex (19). Normal mode analysis of the model complex U(NMe)₂I₂(THF)₃ and of 2 (from DFT calculations) further confirms this (20). With use of this technique, we identified a strong IR active vibrational mode at 1229 cm⁻¹ in complex 1 and one at 1326 cm⁻¹ in complex 2, corresponding to the N-U mode coupled out of phase with the N-C stretch mode (21). The ultraviolet-visible (UV-vis) spectra of 1 and 2 are similar, and each display two intense, broad maxima. For 1, the absorption bands occur at 291 nm (e = 177.4 ± 0.3% and 176.2 ± 0.2%), I and 2 exhibit a trans geometry (N1-U1-N2 = 175.4° ± 0.2°) and very short U-N bonds (U1-N1 = 1.848 ± 0.004 Å and U1-N2 = 1.840 ± 0.004 Å). Both imido ligands are linear (U1-N1-C1 = 167.7° ± 0.3° and U1-N2-C5 = 168.9° ± 0.4°). The bis(imido) unit in 2 is nearly identical to that of 1 (U1-N1 = 1.866 ± 0.002 Å, U1-N2 = 1.859 ± 0.002 Å, N1-U1-N2 = 177.4° ± 0.09°, U1-N1-C1 = 177.7° ± 0.2°, and U1-N2-C7 = 176.2° ± 0.2°). The U-N bonds are significantly shorter than the U-N interactions reported for [PPh₂][UOCl₂(NSPH₂)] and [PPh₂][UOCl₂(NPPh₂)] (1.920 ± 0.003 Å and 1.912 ± 0.003 Å, respectively) (7). The U-N bonds in 1 and 2 are also much shorter than those observed in other uranium imido species, e.g., Cp⁺₄U(NPh) (U-N = 1.952 ± 0.007 Å) (24), Cp⁺₄U(NAd)₂ (average U-N = 1.95 Å) (11), and U[NSiMe₃]₂[N(SiMe₃)]₂ (U-N = 1.910 ± 0.006 Å) (25). Furthermore, the trans arrangement of the imido ligands is rare, even in transition metal chemistry (19, 26, 27).

The optimal structures of U(NMe)₂I₂(THF)₃ and 2 as predicted by DFT calculations agree very well with experiment, with the U-N and U-I bond lengths predicted to within 0.005 Å of the experimental values and the computed N-U-U angle predicted to within 2° (28, 29). The molecular orbitals involved in the U-N bonds for the model complex U(NMe)₂I₂(THF)₃ along with the percentage participation of the uranium orbitals, are shown in Fig. 2 in descending order of orbital energy. The calculations clearly demonstrate the importance of the 5f orbitals in the U-N interaction. Overall, there are six orbitals with strong interactions between the uranium center and the nitrogen ligands, indicating the presence of two triple bonds.

Each of these six orbitals contains a large 5f or 6d component, as indicated in Fig. 2. The top two bonding orbitals correspond to π interactions where the uranium participates in the bonding via the 5f electrons. The following two molecular orbitals also represent π bonds in which the 5f and 6d atomic orbitals of the metal center take part. The remaining two U-N bonding orbitals correspond to two σ interactions with the uranium participation comprised of mostly 5f (mixed with smaller 6d and 6p components) in one and mostly 6d in the other. Overall, the U-N bonding in U(NMe)₂I₂(THF)₃ follows a similar pattern to that of the UO₂⁺³ fragment, which has six bonding orbitals, σ₂⁺, σ₆⁺, two π⁺, and two π₋ (30), although with slightly smaller participation of the uranium orbitals.

In each orbital the uranium contribution is large, indicating a strong covalent interaction. This is consistent with the Mulliken population analysis, which assigns an effective total charge on uranium of +1.50. This contrasts with a completely ionic description in which the formal charge on U(VI) would be +6. Furthermore, the natural bond orbital (NBO) analysis assigns an effective total charge of +1.27. For comparison, an NBO analysis of uranyl assigns a higher charge on uranium of +2.84, indicating a more ionic interaction. Our conclusions are in agreement with those of Kaltsoyannis (4), who carried out an extensive analysis of the six bonding orbitals in the naked U₂N₆ and U(NPR₃)₂⁺⁺ fragments and found that the U-N bonds were more covalent than the analogous U-O interactions in uranyl.

Complexes 1 and 2 are excellent starting materials for the synthesis of new uranium imido complexes; the THF ligands of 1 and 2 are readily displaced by addition of other donor ligands, and addition of alkali metal salts exchanges the iodide groups for other anionic ligands. In addition, the methodology outlined in Scheme 2 appears to be a general reaction, allowing the synthesis of many new uranium imido species by simply
changing the primary amine used in the reaction, thus allowing exceptional sterio- and electronic control at the metal center (*31*). Detailed spectroscopic investigations of compounds 1 and 2 and their derivatives will allow further quantification of the extent of f-orbital participation in the imido interaction.

References and Notes

12. All the calculations were carried out with use of the B3LYP functional. The Stuttgart relativistic effective core potential was used for the uranium atom, and the double zeta basis 6-31G* was used for all the other atoms.
16. Complete details of the synthesis and characterization of 1 and 2 can be found on Science Online.
18. Complex 1 could also be made from U(NMe)2I2(THF)4 in 87% yield.
20. For the computer simulations of complex 1, we used a model system that replaced the Bu* (Bu is tert-butyl) substituents with methyl groups, and the molecules were studied in gas phase. We do not expect this simplification to affect the understanding of the U-N bonding because the predicted bond distances are in very good agreement with the experimental ones. The 0.03 cm⁻¹ difference between the calculated and observed bands that are assigned as having a great deal of U-N stretching character to them is expected given the ability of the DFT method to calculate vibrational frequencies of complex molecules.
23. Crystal data for U[NBu]2J2(THF)2 (1): C25H34J2N2O3U, Mmol = 778.28, monoclinic, P2_1/n, a = 12.3751 ± 0.0007, b = 15.3700 ± 0.0008, c = 24.8084 ± 0.0007, β = 90.507 ± 0.001, V = 2373.7 ± 0.2 Å³, Z = 4. For 5822 reflections and 245 parameters collected at 141 K with F > 2σ(F), R = 0.0288 and wR = 0.0613. Crystal data for U(NP)2J2(THF)2 (2): C24H24J2N2O3U, Mmol = 890.36, monoclinic, P2_1/n, a = 10.8667 ± 0.0008, b = 17.7376 ± 0.0013, c = 14.2243 ± 0.0011, β = 90.070 ± 0.001, V = 2727.0 ± 0.4 Å³, Z = 4. For 6802 reflections and 289 parameters collected at 141 K with F > 2σ(F), R = 0.0181 and wR = 0.0414.
28. The equivalent complex with the iodide ligands in a trans configuration was calculated to have essentially the same energy as complex 1. The U-I bond distances in the trans configuration are longer by 0.02 Å and 0.04 Å with respect to the cis isomer, whereas the U-N bond distances remain almost unaltered.
29. The U-N-C angle in the calculated structure of U(NMe)2I2(THF)4 differs from 180°. However, this angle is known to be easily perturbed and is not a good indicator of the strength of the imido interaction with the metal (32).
31. Initial studies have demonstrated that a variety of substituted aryl amines are viable substrates. The chemistry and characterization of these compounds will be reported in due course.
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Supporting Online Material

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Materials and Methods
Figs. S1 and S2
Tables S1 to S3
References

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