Understanding Geometric Preferences in Uranium(VI) Mixed Tris(imido) Systems

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Insight into Geometric Preferences in Uranium(VI) Mixed Tris(imido) Systems

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Uranium tris(imido) species have been synthesized using different imido groups in the axial and equatorial positions by treating [(^{Mes}PDI^{Me})U(THF)]$_2$ (1-THF), which is a uranium(IV) dimer that is supported by ^{Mes}PDI^{Me} tetraanions, with mixed organoazide solutions. The arrangement of the imido groups is determined by the reduction potentials of the organoazides.

Uranium-nitrogen multiple bonds have become an important subject of study in understanding the electronic structures of actinide compounds due to their ease of synthesis, solubility, and amenability to a number of spectroscopic and structural analytical techniques.[1-6] Molecules containing two uranium-nitrogen multiple bonds, namely *trans*-bis(imido) species, [U(NR)$_2$]$^{2+}$, have been of special interest as they are analogous to ubiquitous uranyl compounds, [UO$_2$]$^{2+}$.[7] Due to their polar nature, uranyl compounds can be plagued by insolubility and/or aggregation, making their bonding and electronic structures difficult to elucidate. The imido analogues have the additional advantage that they are tunable, facilitating reactivity studies and examination of structure-activity relationships.

In 2014, our laboratory reported the synthesis of the first uranium(VI) tris(imido) compounds.[8] These molecules, ^{Mes}PDI^{Me}U(NMes)$_3$ (**2-Mes**) (^{Mes}PDI^{Me} = 2,6-((Mes)N=CMe)$_2$-C$_5$H$_3$N; Mes = 2,4,6-trimethylphenyl) and ^{Mes}PDI^{Me}U(NDipp)$_3$ (**2-Dipp**) (Dipp = 2,6-diisopropylphenyl), were synthesized by treating [(^{Mes}PDI^{Me})U(THF)]$_2$ (**1-THF**), which is a uranium(IV) dimer that is supported by ^{Mes}PDI^{Me} tetraanions, with 6 equiv. of N$_3$Mes or N$_3$DIPP, respectively. During this reaction, the eight stored electrons in both ^{Mes}PDI^{Me} ligands and the four stored electrons in the uranium(IV) *f*^{2} ions serve as potent reductants for the organoazide; thus, an overall 12 electron redox reaction is observed. Structural analysis of these species showed the

trans-imido U=N bonds are elongated in comparison to typical bis(imido) species.[7, 9, 10] Further, the equatorial imido U=N bond is elongated when compared to the *trans* U=N bond due to the Inverse Trans-Influence (ITI).[11-13] Computational analysis of **2-Mes** modeled the structural parameters well, showing that these structural anomalies are due to competition for the 5*f* and 6*d* orbitals by all three imido substituents. The nitrogen from the equatorial imido is also donating electron density to the *fz*^{3} orbital, which participates in σ-bonding with the *trans*-imido substituents along the z-axis, furthering this elongation.

Because the equatorial imido substituent is unique and activated, we reasoned that tris(imido) species with a mixture of imido substituents could be synthesized. We hypothesized that uranium(VI) mixed tris(imido) compounds could be generated by using a combination of organoazides in the reaction with **1-THF**. Herein, we report the synthesis of new uranium(VI) tris(imido) species which feature different imido substituents in the axial and equatorial positions. Structural, spectroscopic, and electrochemical techniques have been used to elucidate the geometric preferences for these mixed tris(imido) derivatives.

Our synthetic efforts began by treating **1-THF** with a pre-mixed solution of 4 equiv. of N$_3$Dipp and 2 equiv. of N$_3$Mes (Scheme 1). After workup and isolation (~80% yield), ^{1}H NMR spectroscopy revealed formation of a new product, tentatively assigned as the mixed tris(imido) species, well as small amounts
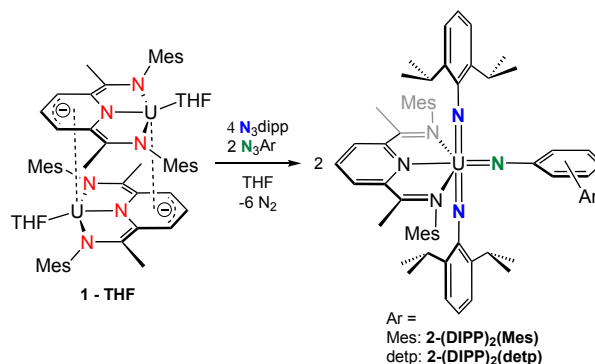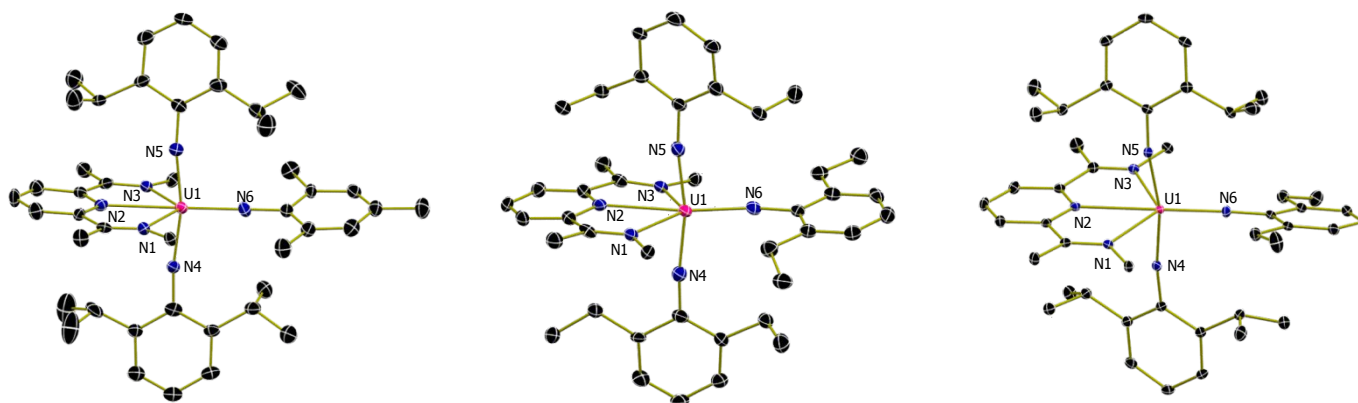
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Figure 1. Molecular structures of **2-(Dipp)₂(Mes)** (left), **2-(Detp)** (centre), and **2-(Dipp)₂(Detp)** (right) shown at 30% probability ellipsoids. Hydrogen atoms and co-crystallized solvent molecules have been omitted for clarity. Mesityl substituents of $^{Mes}PDI^{Me}$ have been truncated to the *ipso* carbon atom for clarity.

of previously identified **2-Dipp**. The spectrum of the new product showed sharp resonances displaying splitting, typical for a diamagnetic compound. However, some unusual shifting was also noted, consistent with temperature independent paramagnetism associated with the uranium(VI) ion.[3]

Resonances for the methyl substituents of the $^{Mes}PDI^{Me}$ ligand are found at nearly identical locations as with **2-Mes** and **2-Dipp**,[8] appearing at 1.71, 2.02, and 2.12 ppm for this new product. Likewise, resonances for the Ar-H protons of the ligand are located at 6.72, 7.24, and 7.79 ppm, similar to **2-Mes** and **2-Dipp**. Dipp imido substituents were identified and have similar peak distributions to those in the axial positions in **2-Dipp**, with two iPrCH₃ signals at 0.71 and 1.53 ppm (12H each), with corresponding iPrCH (2H) resonances at 3.69 and 8.44 ppm. The m-ArH and p-ArH resonances for the Dipp substituent can be found at 7.29 and 5.93 ppm, respectively. These resonances match the assigned resonances in the spectrum of **2-Dipp**. Signals consistent with a Mes imido substituent can be found at 4.41, 5.86, and 8.15 ppm, corresponding to the o-, p-, and m-ArH protons, respectively. These resonances are similar to those assigned to the equatorial imido substituent in **2-Mes**.[8]

To confirm the arrangement of the imido substituents as assigned by ¹H NMR spectroscopy, X-ray crystallography of suitable crystals obtained from a concentrated THF/n-pentane solution cooled to -35 °C was performed (Figure 1, left; Table 1). Analysis revealed the formation of *trans*-($^{Mes}PDI^{Me}$)U(NDipp)₂(NMes) (**2-(Dipp)₂(Mes)**), which is a mixed tris(imido) complex, with two DIPP imido substituents in the axial positions, and a Mes imido group coordinated in the equatorial plane, with the $^{Mes}PDI^{Me}$ ligand completing the pseudo-octahedral coordination environment. Much like in **2-Dipp** and **2-Mes**, the axial imido bonds are slightly bent from linear with a N-U-N bonding angle of 167.9(3)º, and have axial

U=N bond distances of 1.997(7) and 1.967(7) Å. The equatorial imido bond is slightly elongated as expected with respect to the two axial U=N bonds with a distance of 2.027(8) Å, as is observed with the parent complexes, highlighting the ITI. The U-N$_{PDI}$, and intraligand C-N and C-C distances are consistent with a neutral $^{Mes}PDI^{Me}$ ligand formalism.[8, 14-16]

Interestingly, performing the reaction with the opposite ratio of organoazides, 2 equiv. of N₃DIPP and 4 equiv. of N₃Mes, did not produce the inverse, *trans*-($^{Mes}PDI^{Me}$)U(NMes)₂(NDipp). Instead, the predominant species in solution were found to be **2-(Mes)** and **2-(Dipp)₂(Mes)**, in roughly a 2 to 1 ratio. This suggests there is a preference for the formation of **2-(Dipp)₂(Mes)**. Furthermore, in a control experiment where **2-Dipp** and **2-Mes** are mixed, no exchange was found to occur under the reaction conditions, so the mixture in substituents occurs during the synthesis and not after.

To investigate the scope of this reaction, N₃Detp (Detp = 2,6-diethylphenyl) was employed. To ensure the reactivity of this azide was analogous to both N₃Mes and N₃Dipp, the tris(imido), ($^{Mes}PDI^{Me}$)U(Ndetp)₃ (**2-(Detp)**) was initially synthesized by treating **1-THF** with 6 equiv. of N₃Detp. Using the same workup as for **2-(Mes)** and **2-(Dipp)**, **2-(Detp)** was isolated and characterized. The ¹H NMR spectroscopic shifts are as expected based on those previously reported for **2-(Mes)** and **2-(Dipp)**. X-ray crystallographic characterization was performed on crystals obtained from a concentrated THF solution layered with n-pentane at -35° C and showed a structure analogous to **2-(Mes)** and **2-(Dipp)** (Figure 1, centre; Table 2). As for these structures, the imido in the equatorial position (2.028(8) Å) is slightly longer than those in the axial positions (1.967(7), 1.996(6) Å). Again, the U-N$_{PDI}$, and intraligand C-N and C-C distances as expected for a neutral $^{Mes}PDI^{Me}$ ligand.

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Table 1. Metrical Parameters for **2-Detp, 2-(Dipp)₂(Mes), 2-(Dipp)₂(Detp).** Bonds are listed in Angstroms (Å), angles listed in degrees (°).

	2-Detp	2-(Dipp)₂(Mes)	2-(Dipp)₂(Detp)
U1-N4	1.989(7)	1.967(7)	1.987(3)
U1-N5	1.970(7)	1.996(6)	1.988(3)
U1-N6	2.030(7)	2.028(8)	2.033(3)
N4-U1-N5	168.4(3)	167.9(3)	167.13(12)
N4-U1-N6	96.6(3)	95.9(3)	96.75(12)
N5-U1-N6	95.0(3)	96.2(3)	96.11(12)

With **2-(Detp)** established, the analogous experiment to form mixed tris(imido) species was performed by adding a premixed solution of 4 equiv. of N_3Dipp and 2 equiv. of N_3Detp to **1-THF**, which gave similar results as in the case of **2-(Dipp)₂(Mes)**. Analysis by ^{1}H NMR spectroscopy showed a spectrum that was consistent with the formation of *trans*-(^{Mes}PDI^{Me})U-(NDipp)₂(NDetp) (**2-(Dipp)₂(Detp)**). Resonances for *trans*-DIPP imido groups were visible in the expected range, and new resonances for the ethyl groups of Detp in the equatorial position were also observed. As in the case of **2-(Dipp)₂(Mes)**, reversing the ratio of organoazides did not produce the opposite mixed product, *trans*-(^{Mes}PDI^{Me})U(NDetp)₂(NDipp). The solution showed mainly formation of **2-Detp** with some **2-(Dipp)₂(Detp)** present.

The geometry of **2-(Dipp)₂(Detp)** was further corroborated by X-ray diffraction of crystals obtained from a concentrated THF solution layered with *n*-pentane (-35 °C) (Figure 1 right; Table 1). Analysis revealed two DIPP imido fragments which are in a *trans* orientation in the axial positions with U=N$_{imido}$ bond lengths (1.987(3), 1.988(3) Å) similar to those observed for **2-(Dipp)₂(Mes)**. The third imido ligand, N-Detp, is bound in the equatorial plane trans to ^{Mes}PDI^{Me} featuring a longer U=N$_{imido}$ bond length (2.033(3) Å) as compared to the DIPP imidos in the axial positions. This is a similar elongation to that seen in **2-(Dipp)₂(Mes)**, consistent with the ITI. The U-N$_{imine}$ (2.564(3), 2.558(3) Å) and U-N$_{pyr}$ (2.589(3) Å) distances for the ^{Mes}PDI^{Me} are consistent with those in **2-(Dipp)₂(Mes)**.

Based on the observed arrangement of the three imido substituents in **2-(Dipp)₂(Mes)** and **2-(Dipp)₂(Detp)**, where the NDipp groups are preferentially located in the axial positions, a steric argument can be invoked to explain imido group placement. It is possible that the smaller substituent is favored in the equatorial plane to avoid interaction with the Mes groups on ^{Mes}PDI^{Me} ligand. Examination of the crystal structures supports this, where the closest contact of the mesityl substituent in **2-(Dipp)₂(Mes)** to the Mes on ^{Mes}PDI^{Me} is ~3.4 Å, but only ~3.0 Å for the ethyl of **2-(Dipp)₂(Detp).** The fact that no equilibria were observed during formation of the tris(imido) derivatives and no imido crossover was noted in control experiments further supports a kinetic preference to imido group placement.

We also hypothesized that the geometric preference could be driven by an electronic effect of the aryl substituent on the organoazide. Qualitatively, there should be a difference between N_3Dipp, N_3Mes, and N_3Detp in terms of their relative ease of reduction, which can be explained using the inductive effects of the respective isopropyl, methyl, and ethyl

substituents on the phenyl ring. To explore this quantitatively, the ease of activation of each of the organoazides was assessed using cyclic voltammetry, with reduction potentials being measured against an internal standard of Fc/Fc⁺. These cyclic voltammograms show two-electron irreversible reduction of organoazides, consistent with loss of N_2 upon activation (Table 2).

Table 2. Electrochemical data for organoazides.

Azide	Reduction potential (V)*
2,6-diisopropylphenyl (Dipp)	-2.942
2,4,6-trimethylphenyl (Mes)	-2.816
2,6-diethylphenyl (Detp)	-2.746

* c.a. 0.01 M Fc/Fc⁺ standard, all runs at 100 mVs⁻¹; Electrolyte: 0.2 M [^{n}Bu₄N][PF₆] in 3 mL THF; Azides: 0.005 M - 0.01 M.

The electrochemical data shows that measured reduction potentials trend well with what would be expected based on the electron donating ability of alkyl substituents on the phenyl rings. This analysis suggests that the imido group with the more electron donating substituents, those with the more negative reduction potentials, trend towards the axial position, forming a *trans*-bis(imido) arrangement. This likely occurs because these imido groups are poorer oxidizers compared to their more electron withdrawing counterparts. Thus, the more oxidizing groups, those with the more positive reduction potentials, are preferred in the equatorial position.

To rationalize this trend, the bonding that was elucidated from the electronic structure of **2-Mes** must be examined. As previously mentioned,[8] the equatorial imido substituent donates electron density to the *f*z³ orbital, which in turn causes elongation along the z-axis. Additional electron density from more electron donating substituents along the equatorial vector will cause further interruption to the ITI, which is thermodynamically disfavored. Therefore, it is preferred to have the more oxidizing (electron withdrawing) substituents, which siphon electron density away from the *f*z³, in the equatorial position. Using a more oxidizing group in the equatorial position, such as Mes or Detp as compared to a Dipp group, is favorable as it will minimize the destabilization of the ITI along the *f*z³ axis.

Conclusions

In summary, formation of uranium(VI) tris(imido) species with variation in the imido substituents is possible using mixed solutions of organoazides. Aryl groups substituted with either methyl-, ethyl-, or isopropyl- substituents were used successfully to generate this new family of tris(imido) derivatives with mixed substituents. While the origin of the preference is not immediately clear, both steric and electronic arguments can be made to explain the observed geometric arrangement of imido groups. Future studies will be aimed at further varying the substituents to aliphatic groups.

Conflicts of interest

There are no conflicts to declare.

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Exploring Geometric Preferences in Uranium-Tris(Imido) Systems
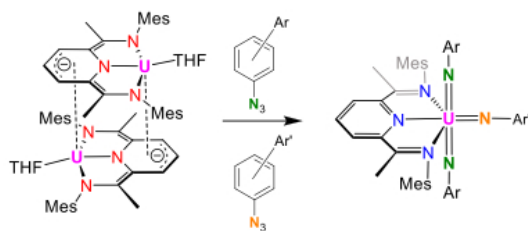
How does the azide choice
affect imido formation?

Axial vs. Equatorial

338x190mm (54 x 54 DPI)