

DFT and CASPT2 Analysis of Polymetallic Uranium Nitride and Oxide Complexes: How Theory Can Help When X-Ray Analysis Is Inadequate

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Abstract: Recent studies of organouranium chemistry have provided unusual pairs of similar polymetallic molecules containing (N)³⁻ and (O)²⁻ ligands, namely [(C₅Me₅)U(μ-l)₂]₃(μ₃-N), **1**, and [(C₅Me₅)U(μ-l)₂]₃(μ₃-O), **2**, and chair and boat conformations of [(C₅Me₅)₂U(μ-N)U(μ-N₃)(C₅Me₅)₂]₄, **3**. These compounds were analyzed by density functional theory and multiconfigurational quantum chemical studies to differentiate nitride versus oxide in molecules for which the crystallographic data were not definitive and to provide insight into the electronic structure and unique chemical bonding of these polymetallic compounds. Calculations were also performed on [(C₅Me₅)₂UN₃(μ-N₃)]₃, **4**, and [(C₆F₅)₃BNU(N[Me]Ph)₃], **5**, for comparison with **1** and **3**. On the basis of these results, the complex, [(C₅Me₅)U(μ₃-E)]₈, **6**, for which only low-quality X-ray crystallographic data are available, was analyzed to predict if E is nitride or oxide.

Introduction

The synthesis of polymetallic uranium nitrides¹ is of interest since molecules dense in uranium and nitrogen could function as molecular precursors to high-purity UN, a potential nuclear fuel due to its high melting point, density, and thermal conductivity.^{2,3} Attachment of nitride ions, N³⁻, to uranium is also of interest with respect to the nature of multiple bonding when 5f valence orbitals of actinide metals are involved. However, only a few uranium nitrides are known. Although synthesis of such complexes is challenging, characterization is not always straightforward since in some cases it is difficult to differentiate between the presence of a nitride and an oxide ligand. In X-ray crystallographic experiments, it is often difficult to reliably identify N vs O in the presence of heavy metals such as uranium. Since uranium has several available oxidation states, simple charge balance also does not provide a differentiation. Magnetic analysis of polymetallic uranium complexes also can be complicated. ¹⁵N labeling is often the only way to definitively identify nitride vs oxide components, but this depends on the availability of the requisite ¹⁵N-labeled precursors, the success of the synthetic method, and the ability to analyze the complex by mass spectrometry.

Quantum chemical calculations on actinide-containing systems, on the other hand, are challenging mainly because of the

complexity of the electronic structure of the actinide atoms. One needs a method that describes properly electron correlation effects⁴ as well as relativistic effects.⁵ In other words, the method used to describe the electronic structure of such compounds must be relativistic and must have the capability to describe complex electronic structures where the wave functions have a strong multiconfigurational nature. One of the most successful multideterminantal approaches is to determine a reference wave function with the complete active space self-consistent field (CASSCF) method,⁶ where the wave function is described as a combination of different electronic configurations, and then account for additional electron correlation effects using a multiconfigurational second-order perturbation theory, e.g., CASPT2.⁷ The CASSCF/CASPT2 method has been demonstrated to provide accurate results for ground and electronically excited states of molecules containing atoms throughout the entire periodic table.

It was of interest to determine if theoretical methods could be useful in differentiating nitride versus oxide in polymetallic uranium complexes. If computational methods are sufficiently precise, they can provide better data than is obtainable experimentally. In any case, they may provide insight into the characteristics of nitride vs oxide compounds such that experimental methods could be used to identify which main group element is present.

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Recently, two pairs of similar polymetallic uranium complexes $[(C_5Me_5)U(\mu-I)_2]_3(\mu_3-N)$, **1**,⁸ and $[(C_5Me_5)U(\mu-I)_2]_3(\mu_3-O)$, **2**,⁹ have been synthesized that provide the opportunity to evaluate the capacity for theoretical methods to handle such nitride and oxide molecules. Here, we present a combined density functional theory and multiconfigurational quantum chemical study on these compounds. In addition, the trimetallic U(IV) complex $[(C_5Me_5)_2UN_3(\mu-N_3)]_3$, **4**,⁸ was chosen to expand the study of U–N(azide) bonding, whereas $(C_6F_5)_3BNU(N[Me]Ph)_3$, **5**,¹⁰ was selected to further examine U–N(nitride) bonding. On the basis of the results, a polymetallic uranium complex of uncertain composition based on X-ray data was analyzed to evaluate the likelihood that nitride was present and to determine if it was worthwhile to pursue further studies on this compound.

Computational Details

Density functional theory (DFT) geometry optimizations of the experimentally synthesized $[(C_5Me_5)U(\mu-I)_2]_3(\mu_3-N)$,⁸ $[(C_5Me_5)U(\mu-I)_2]_3(\mu_3-O)$,⁹ $[(C_5Me_5)_2UN_3(\mu-N_3)]_3$,⁸ $[(C_5Me_5)U(\mu_3-N)]_8$, and $[(C_5Me_5)U(\mu_3-O)]_8$ structures as well as the boat and chair conformations of $[(C_5Me_5)_2U(\mu-N)U(\mu-N_3)(C_5Me_5)_2]_4$ ¹¹ were performed with the Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional¹² and triple- ζ valence plus polarization (def-TZVP) basis sets on all atoms. Quasi-relativistic pseudopotentials were used for I and U atoms, with 46 and 60 core electrons, respectively.^{13–15} Spin density was computed by means of natural bond order (NBO) analysis. All DFT calculations were performed using the broken symmetry option (unrestricted calculations). The TURBOMOLE 5.10 program package was employed.¹⁶

Multiconfigurational complete active space (CASSCF)⁶ calculations followed by second-order perturbation theory (CASPT2)⁷ were performed at the DFT-optimized geometries of $[(C_5Me_5)U(\mu-I)_2]_3(\mu_3-N)$, $[(C_5Me_5)U(\mu-I)_2]_3(\mu_3-O)$, and $[(C_5Me_5)_2UN_3(\mu-N_3)]_3$ in which for simplicity the Me groups were replaced by H in the $(C_5Me_5)^-$ ligands. The calculations on the $[(C_6F_5)_3BNU(N[Me]Ph)_3]$ complex were performed at the DFT-optimized structure of ref 10. Scalar relativistic effects were included using the Douglas–Kroll–Hess Hamiltonian¹⁷ and the relativistic all electron ANO-RCC basis sets¹⁸ with double- ζ quality (ANO-RCC-VDZP) with the following contractions: [8s7p5d3f1g] for U, [3s2p1d] for N, O, and B, and [6s5p3d1f] for I. The ANO-RCC-MB basis set was employed on F, C, and H with a contraction of [2s1p] for C and F and [1s] for H. Spin–orbit coupling effects were computed by using the CASSCF State Interaction (CASSI) method,^{19,20} in which an effective one-electron spin–orbit Hamiltonian based on the atomic mean field approximation of the two-electron part was employed. The active space contains six electrons ($[(C_5Me_5)U(\mu-I)_2]_3(\mu_3-N)$, **1**, and $[(C_5Me_5)_2UN_3(\mu-N_3)]_3$, **4**) and seven electrons

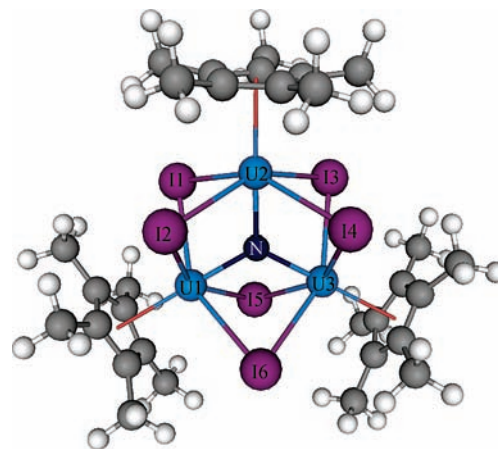


Figure 1. DFT-optimized structure of $[(C_5Me_5)U(\mu-I)_2]_3(\mu_3-N)$: U, blue; N, dark blue; I, violet; C and H, dark gray and white, respectively.

Table 1. Selected Bond Distances (Å) and Angles (deg) for $[(C_5Me_5)U(\mu-I)_2]_3(\mu_3-N)$, **1**

	PBE/TZVP	experiment
U1–Cnt1	2.471	2.455
U2–Cnt2	2.471	2.462
U3–Cnt3	2.469	2.457
U1–N	2.145	2.152(3)
U2–N	2.149	2.138(3)
U3–N	2.154	2.157(3)
U1–I1	3.186	3.1536(4)
U1–I2	3.183	3.1599(4)
U1–I5	3.181	3.1720(4)
U1–I6	3.183	3.1599(4)
U2–I3	3.197	3.1632(4)
U2–I4	3.175	3.1617(4)
U2–I1	3.185	3.1586(4)
U2–I2	3.184	3.2109(4)
U3–I5	3.187	3.1825(4)
U3–I6	3.194	3.1622(4)
U3–I3	3.194	3.1648(4)
U3–I4	3.174	3.1483(4)
U2–U3–U1	59.869	59.985(8)
U2–U1–U3	60.083	59.710(4)
U3–U2–U1	60.048	60.305(6)
Cnt1–U1–N	179.5	178.1
Cnt2–U2–N	179.3	178.6
Cnt3–U3–N	178.8	178.1

$[(C_5Me_5)U(\mu-I)_2]_3(\mu_3-O)$, **2**) in 21 orbitals, which are linear combinations of the 5f orbitals of the three U atoms. For $[(C_6F_5)_3BNU(N[Me]Ph)_3]$, the most adequate active space comprises 14 electrons arising from the U and N atoms distributed in 14 orbitals (14/14), which are linear combinations of the 6d/5f orbitals of U and 2p of N. The CASSCF/CASPT2 calculations were performed with the MOLCAS 7.3 package.²¹ This approach has been successful in studying many actinide-containing systems.^{22–31} The computational costs arising from the two-electron integrals were drastically reduced by employing the Cholesky decomposition (CD) technique in all CASSCF/CASPT2 calculations^{32–34} combined with the Local Exchange (LK) screening.³⁵

Results

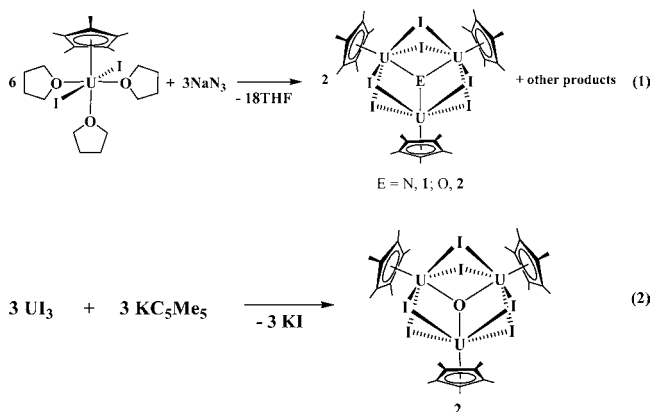
$[(C_5Me_5)U(\mu-I)_2]_3(\mu_3-N)$, **1**, vs $[(C_5Me_5)U(\mu-I)_2]_3(\mu_3-O)$, **2**. NaN_3 reacts with trivalent $(C_5Me_5)UI_2(THF)_3$ to generate a product identified by X-ray crystallography as $[(C_5Me_5)U(\mu-I)_2]_3E$, eq

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1.⁸ If E were a nitride, this would be a U^{4+} complex formed by U^{3+} conversion of azide to nitride. However, E could be oxide derived from an adventitious source of oxygen, and the complex could be a $(U^{4+})_2(U^{3+})$ mixed valence compound. It was also possible that E could be hydroxide, and a $(U^{4+})(U^{3+})_2$ mixed valence combination of metals was present. Mass spectroscopic analysis of a product made from $Na(^{15}N=N=N)$ indicated that E was nitride, not oxide, as shown in eq 1.

Subsequently, the oxide analogue of **1** was reported according to eq 2.⁹ Fortunately, $[(C_5Me_5)U(\mu-I)_2]_3(\mu_3-O)$, **2**, had a different color, crystallographic space group ($P2_1/n$, **1** vs $P2_1/c$, **2**), and NMR spectrum from **1**; i.e., these are two different complexes.



However, this pair emphasizes the possibility that central atoms in polymetallic uranium complexes can be nitride or oxide.

Computational studies on both complexes were undertaken in order to differentiate between the two structures: nitride vs oxide. The DFT-optimized structure of complex **1** is visualized in Figure 1, and selected bond distances and angles are listed in Table 1. The optimized geometry is in very good agreement with the experimental X-ray data. The skeleton of U, I, and N atoms has approximately D_{3h} symmetry. The three U–Cnt atoms has approximately D_{3h} symmetry. The three U–Cnt distances have the same bond length of 2.47 Å (2.46(2) Å exp). The three U–N bond lengths are also the same, 2.145, 2.149, and 2.154 Å (2.138(3), 2.152(3), and 2.157(3) Å exp), suggesting the same oxidation state of the U centers. The fact that the three U centers in $[(C_5Me_5)U(\mu-I)_2]_3(\mu_3-N)$ are equivalent is evident from the spin density analysis at both DFT and CASSCF/CASPT2 levels of theory. They are U(IV) centers,

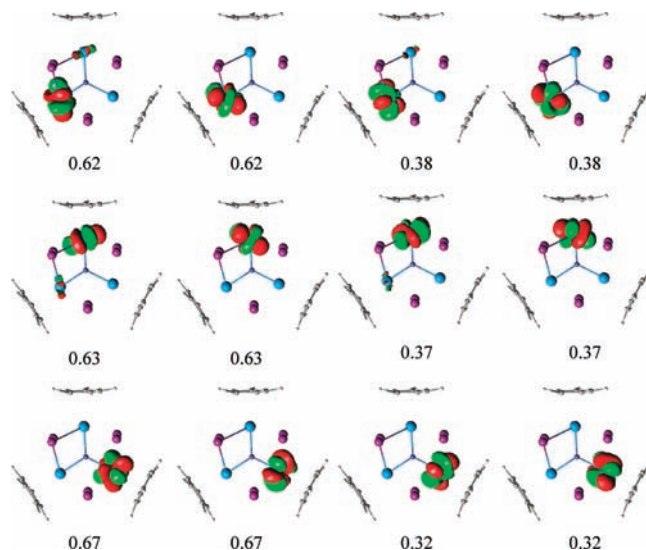


Figure 2. Natural orbitals and their occupation numbers for structure **1**.

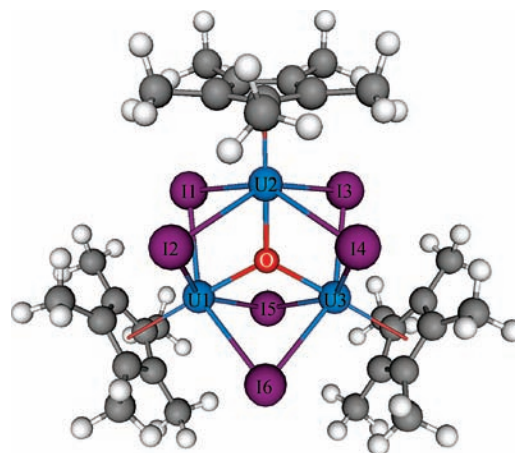


Figure 3. DFT-optimized structure of $[(C_5Me_5)U(\mu-I)_2]_3(\mu_3-O)$: U, blue; O, red; I, violet; C and H, dark gray and white, respectively.

each one having two unpaired electrons in 5f orbitals. Hence, complex **1** is a U(IV) nitride, confirming the experimental suggestion.

At a CASPT2 level, the lowest spin states are 8 septets, 16 quintets, 24 triplets, and 8 singlets, which are almost degenerate in energy. The multiconfigurational nature of this system is evident from the natural orbitals which are linear combinations of the 5f orbitals of the three U centers and their occupation numbers (Figure 2). Twelve of the 21 orbitals have an occupation number that is either 0.32–0.38 or 0.62–0.67 (see Figure 2), while the remaining nine are empty.

The DFT-optimized structure of $[(C_5Me_5)U(\mu-I)_2]_3(\mu_3-O)$, **2**, is presented in Figure 3 and selected bond distances and angles are listed in Table 2. The geometry of **2** is also in good agreement with the experimental X-ray data reported in ref 9 (see also Table 2). As in complex **1**, the three U–Cnt bond distances have the same bond lengths, 2.45 Å (exp 2.44(2), 2.45(2), 2.46(2) Å). The U–O bond lengths are 2.193, 2.203, and 2.208 Å (exp 2.19(1), 2.23(1), 2.23(1) Å), being longer than the U–N ones (2.145, 2.149, and 2.154 Å). This is the only difference concerning the geometries of the two complexes originating from the presence of N or O.

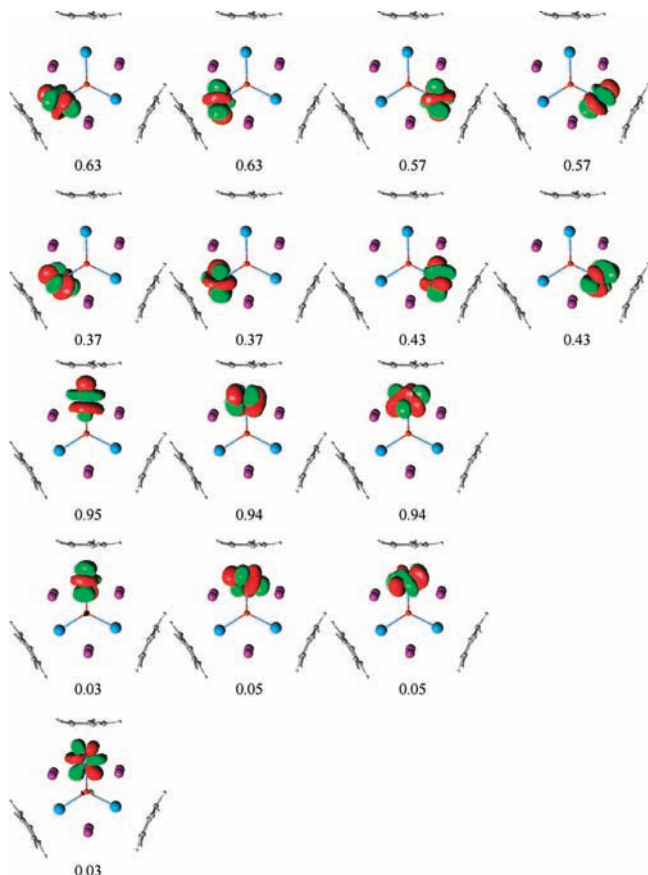
The ground state of system **2** is an octet state almost degenerate with the quartet, whereas the sextet state is 3.5 kcal/

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Table 2. Selected Bond Distances (Å) and Angles (deg) for $[(C_5Me_5)U(\mu-I)_2]_3(\mu_3-O)$, **2**

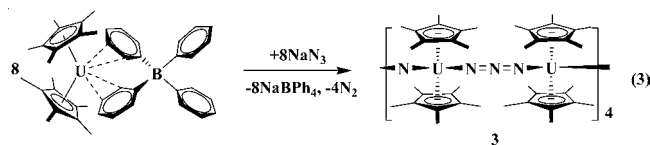
	PBE/TZVP	experiment
U1–Cnt1	2.450	2.450
U2–Cnt2	2.450	2.460
U3–Cnt3	2.447	2.440
U1–O	2.208	2.234
U2–O	2.203	2.192
U3–O	2.193	2.228
U1–I1	3.189	3.214
U1–I2	3.201	3.177
U1–I5	3.198	3.226
U1–I6	3.213	3.198
U2–I3	3.201	3.190
U2–I4	3.206	3.182
U2–I1	3.197	3.179
U2–I2	3.200	3.258
U3–I5	3.195	3.154
U3–I6	3.207	3.181
U3–I3	3.194	3.183
U3–I4	3.211	3.174
U2–U3–U1	59.54	
U2–U1–U3	60.222	
U3–U2–U1	60.239	
Cnt1–U1–O	178.4	176.7(5)
Cnt2–U2–O	178.1	178.0(3)
Cnt3–U3–O	179.5	177.7(3)

mol higher in energy. Again, the natural orbitals (shown in Figure 4) are linear combinations of the 5f orbitals of the three U centers. Both structures are very ionic in nature, and the electrons are localized only on the uranium atoms with no uranium–nitride or uranium–oxo interaction. NBO analysis indicates that the broken-symmetry DFT calculation delocalizes

**Figure 4.** Natural orbitals and their occupation numbers for structure **2**.

the spin density over the three U centers, giving ca. 2.3 on each U. This is a typical example of self-interaction error in DFT, which often leads to over density delocalization.³⁶ On the other hand, the CASSCF/CASPT2 calculations reveal spin densities of 2.96, 1.99, and 1.99 for the octet state, and 2.62, –1.16, and 1.50 for the quartet state (2.84, 0.66, and 1.46 for the sextet state). Thus, in contrast to $[(C_5Me_5)U(\mu-I)_2]_3(\mu_3-N)$, the three U centers in $[(C_5Me_5)U(\mu-I)_2]_3(\mu_3-O)$ are not equivalent: one U is assigned to U(III) and the other two U to U(IV). Therefore, complex **2** is a mixed valence oxide.

Chair versus Boat $[(C_5Me_5)_2U(\mu-N)U(\mu-N_3)(C_5Me_5)_2]_4$, **3.** The reaction of sodium azide with the U^{3+} complex, $[(C_5Me_5)_2U][(\mu-Ph)_2BPh_2]$, produced a mixed azide nitride complex, $[(C_5Me_5)_2-U(\mu-N)U(\mu-N_3)(C_5Me_5)_2]_4$, **3**, eq 3.¹¹ This compound crystallizes with a 24 atom (UNUNNN)₄ ring. Several X-ray crystallographic analyses indicated that this ring could crystallize both in a pseudoboat and a pseudochair form, using the descriptors common with cyclohexane rings, Figure 5. DFT analyses of each conformer of **3** were conducted. CASSCF/CASPT2 calculations, on the other hand, are not affordable for such complex molecules as they would require the use of active space comprising 16 electrons (two electrons per U(IV) center) distributed in 56 orbitals that are linear combinations of the 5f orbitals on each uranium. The two conformations, boat and chair, are very flexible in their geometries. The DFT calculations favor the boat structure by only ca. 5 kcal/mol. The ground state contains 16 unpaired electrons: two electrons per U(IV) center. The chair conformation is a local minimum. If one slightly distorts this structure it converges to the lower energy boat structure. The calculated molecular structure of the boat is in a fairly good agreement with the structure determined experimentally as evident from Table 3. The U–N(azide) bond lengths are computed to be shorter by ca. 0.09 Å than the experimentally measured distances and the U–N–N and N–U–N(azide) angles involving the azide nitrogens differ by ca. 15° from the corresponding X-ray values.



$[(C_5Me_5)_2UN_3(\mu-N_3)]_3$, **4**. Complex **4**, made from $(C_5Me_5)_2-UCl_2$ and NaN_3 ,⁸ was chosen because of its complex uranium azide nature. Each uranium atom is attached to two bridging azide ligands and one terminal azide. Thus, this trimetallic U(IV) complex can provide valuable insight into the nature of the U–N(azide) bonding existing also in the two isomers of $[(C_5Me_5)_2U(\mu-N)U(\mu-N_3)(C_5Me_5)_2]_4$, for which, however, electronic structure calculations are not affordable. Additionally, as the quality of the diffraction experiment was not sufficient for detailed structural analysis,⁸ theoretical calculations are very useful for the structure verification. The DFT-optimized geometry is shown in Figure 6, and selected bond distances and angles are listed in Table 4. The calculated molecular structure is in fairly good agreement with the experimental X-ray structure. As for system **3**, the main discrepancies with the experimental results are in the U–N(azide) bond lengths and the U–N–N angles. The results suggest that eventually DFT fails to capture adequately some aspect of the U–N(azide) bonding.

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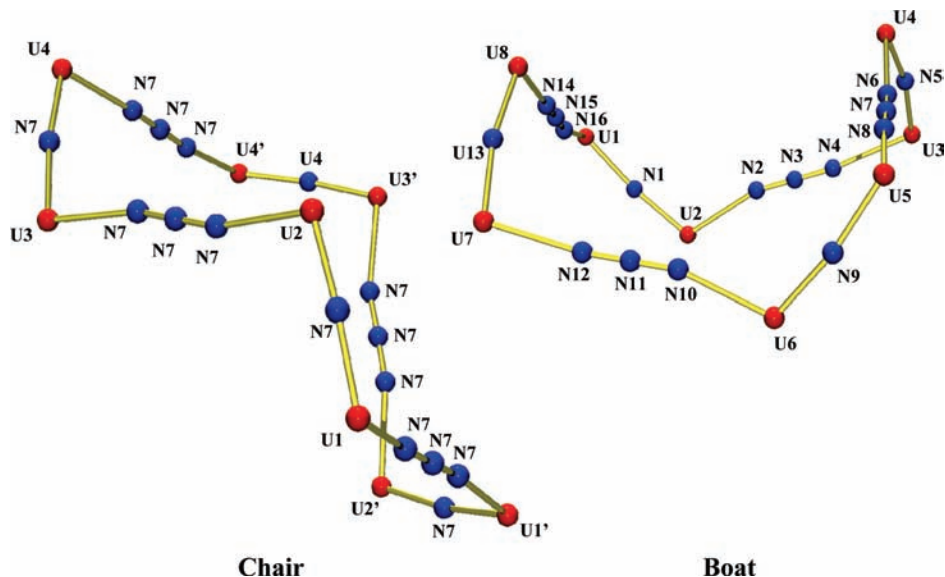


Figure 5. Ball-and-stick representation of the (UNUNNN)₄ rings of isomers of [(C₅Me₅)₂U(μ-N)U(μ-N₃)(C₅Me₅)₂]₄: left, pseudochair observed; right, pseudoboat observed.¹¹

Table 3. Selected Bond Distances (Å) and Angles (deg) for [(C₅Me₅)₂U(μ-N)(C₅Me₅)₂U(μ-N₃)]₄, **3** (Boat Conformation)

	PBE/TZVP	experiment
U–N(nitride)	2.040–2.046	2.047(6)–2.078(6)
U–N(azide)	2.383–2.387	2.476(7)–2.525(7)
U–C(Cp)	2.706–2.795	2.707(8)–2.860(9)
U–Cnt	2.469–2.475	2.488–2.528
U–N–U	166.9–173.0	166.6(4)–168.5(4)
U–N–N	174.8–178.9	160.8(6)–176.7(6)
N–U–N(azide)	99.2–100.8	102.8(2)–110.2(2)
N–N–N	179.9–180.0	178.2(9)–179.3(8)
Cnt–U–Cnt	123.0–124.3	127.4–129.0

Table 4. Selected Bond Distances (Å) and Angles (deg) for [(C₅Me₅)₂UN₃(μ-N₃)]₃, **4**

	PBE/TZVP	experiment
U–N(bridging)	2.343–2.437	2.401(13)–2.446(12)
U–N(terminal)	2.231	2.258(14)–2.283(14)
N–N(bridging)	1.171/1.185	1.143(15)–1.182(15)
N–N(terminal)	1.157/1.207	1.15(2)–1.206(18)
U–Cnt	2.459–2.471	2.444–2.455
U–N–N	164.8–178.9	147.3(13)–169.7(19)
N–U–N	73.3–79.8	71.2(4)–79.1(5)
N–N–N	179.6–180	177(3)–180(2)
Cnt–U–Cnt	123.1–127.7	139.2–140.9

CASSCF/CASPT2 calculations were performed on the DFT-optimized structure in which for simplicity the Me groups were replaced by H in the (C₅Me₅)[−] ligands. Various spin multiplicities were investigated. The lowest spin states are eight septets and eight quintets which are almost degenerate in energy.

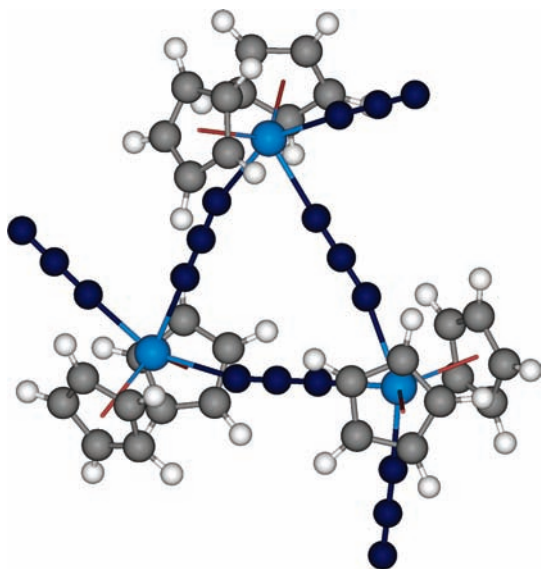


Figure 6. DFT-optimized structure of [(C₅Me₅)₂UN₃(μ-N₃)]₃: U, blue; N, dark blue; C and H, dark gray and white, respectively.

Inclusion of spin–orbit coupling in the treatment spreads out the range of the energies (12 states within 0.5 eV). The lowest state is mainly a septet. As systems **1** and **2**, complex **4** is very ionic in nature and the electrons are highly localized on the U atoms (see Figure 7). The calculations show no U–N covalent interaction. Our results suggest that polimetallc uranium complexes with uranium in formal oxidation state III or IV are bound ionically to azide, nitride, or oxide.

[(C₆F₅)₃BNU(N[Me]Ph)₃], **5**. Choosing a uranium nitride less complicated than **3** for investigating the U–N type of bonding was challenging since such species are limited to binary uranium nitrides like UN and NUN and the ternary nitride, NUF₃.^{37,38} However, recently the first nitridoborate complex of uranium, [(C₆F₅)₃BNU(N[*t*-Bu]Ar)₃], also viewed as borane-capped uranium nitride, has been synthesized and characterized.¹⁰ It has a nearly linear B–N≡U core with U–N bond length of 1.880 Å, which is ca. 0.3 Å shorter than the U–N distances in the [(C₅Me₅)U(μ-I)₂]₃(μ₃-N) system. On the basis of DFT calculations of the U–N bond multiplicity indices on a simplified model [(C₆F₅)₃BNU(N[Me]Ph)₃] (see Figure 8), it was suggested that the system is an analogue of the formally triply bonded U(VI) organoimido complexes, with a bond multiplicity value that is slightly less (2.83) than that of a full triple bond.¹⁰

(37) Kushto, G. P.; Souter, P. F.; Andrews, L. *J. Chem. Phys.* **1998**, *108*, 7121–7130.

(38) Andrews, L.; Wang, X. F.; Lindh, R.; Roos, B. O.; Marsden, C. J. *Angew. Chem., Int. Ed.* **2008**, *47*, 5366–5370.

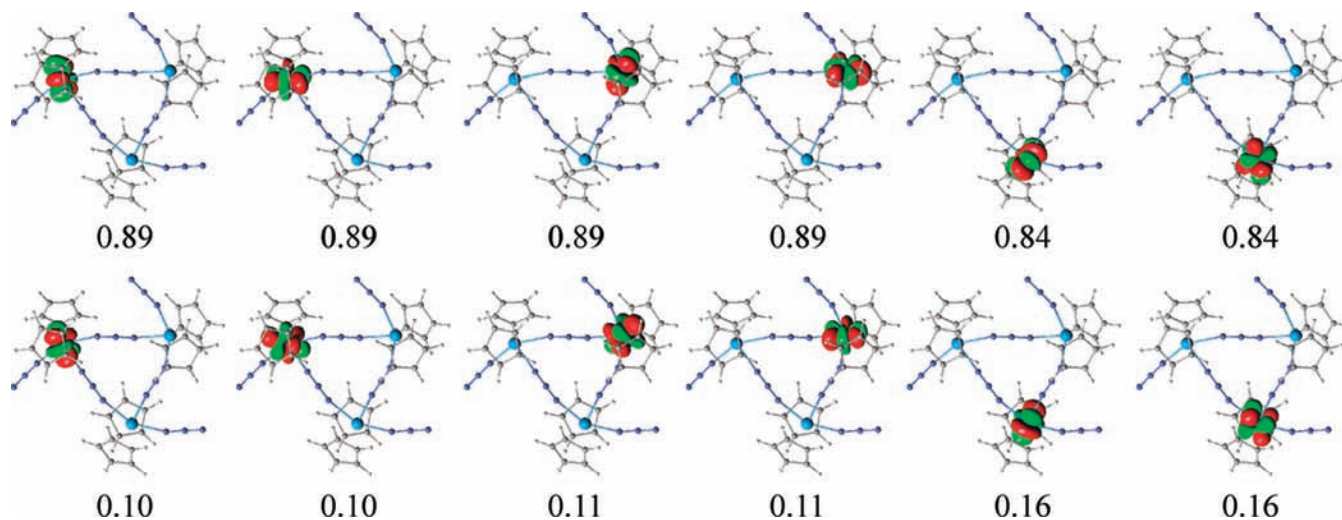


Figure 7. Natural orbitals and their occupation numbers for structure 4.

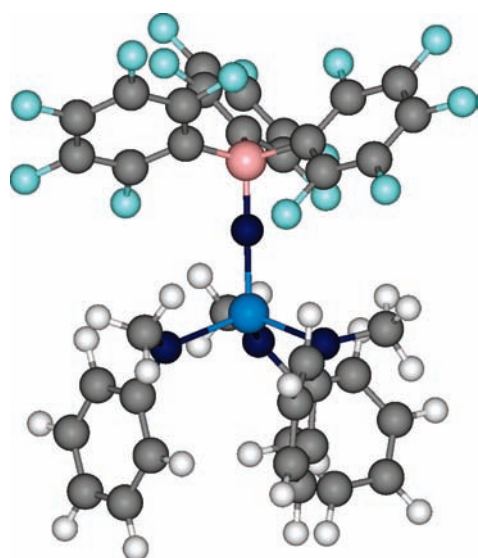


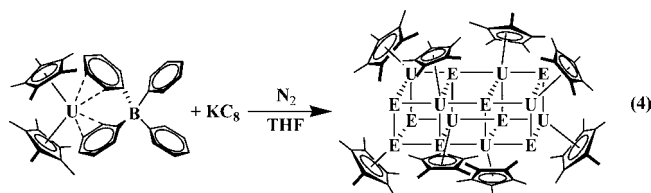
Figure 8. $[(C_6F_5)_3BNU(N[Me]Ph)_3]$ compound: U, blue; N, dark blue; B, pink; F, turquoise; C and H, dark gray and white, respectively.

We have performed multireference calculations at the DFT-optimized structure $[(C_6F_5)_3BNU(N[Me]Ph)_3]$ of ref 10 in order to investigate the U–N type of bonding and to compare it with the bonding in $[(C_5Me_5)U(\mu-I)_2](\mu_3-N)$, **1**, and $[(C_5Me_5)_2U(\mu-N)U(\mu-N_3)(C_5Me_5)_2]_4$, **3**. The ground state is a singlet, which is 49.5 kcal/mol more stable than the triplet state. The natural orbitals and their occupation numbers are shown in Figure 9.

An interesting result is that the U–N orbitals from the B–N≡U core are a σ/σ^* pair of bonding and antibonding orbitals with occupation numbers of 1.97 and 0.03, respectively, as well as two π bonding and their corresponding π^* antibonding orbitals, with occupations of 1.89 and 0.11, respectively. The remaining orbitals encompass the uranium atom and the other three nitrogens. This monouranium complex has uranium in a formal oxidation state VI and contains a covalent triple U–N bond; i.e., it has much more pronounced covalent character than any of the structures **1**, **2** and **4**.

$[(C_5Me_5)U(\mu_3-N)]_8$ vs. $[(C_5Me_5)U(\mu_3-O)]_8$, **6**. Given the success of the DFT method on **1–4**, the analysis of a complex of unknown composition was conducted. The reaction of $[(C_5Me_5)_2U][(\mu-Ph)_2BPh_2]$, the precursor above, with potassium

graphite, KC_8 , in a nitrogen atmosphere generated a complex of formula $[(C_5Me_5)U(\mu_3-E)]_8$, **6**, eq 4. The identity of E could not be determined by X-ray crystallography. Hence, this



compound could be a U^{4+} nitride complex, $E = N$, or it could be a U^{3+} oxide complex where $E = O$. It could also be a mixed oxide/nitride with a mixture of uranium valences. Unfortunately, single crystals of this compound have not been subsequently obtainable so that further characterization by mass spectroscopy, NMR, chemical analysis, and ^{15}N labeling has not been possible.

To determine if the $E = N$ option is viable for **6**, DFT calculations on both $[(C_5Me_5)U(\mu_3-N)]_8$, **6-N**, and $[(C_5Me_5)U(\mu_3-O)]_8$, **6-O**, were performed. In the case of **6-N**, the calculations predicted a structure that matches closely to that determined by X-ray crystallography, Table 5. The U–E bond distances are in the range of 2.145–2.359 Å for $E = N$ and 2.184–2.499 Å for $E = O$ (2.23(2)–2.40(2) Å exp). We observed the same trend as for compounds **1** and **2**; namely, the U–N bonds are shorter than the U–O bonds. Additionally, the U–C_{nt} bond lengths are affected, being slightly shorter for the oxygen-containing analogue (see Table 5). The ground state of $[(C_5Me_5)U(\mu_3-N)]_8$, **6-N**, contains 16 unpaired electrons (two per each U(IV) center), whereas the ground state of $[(C_5Me_5)U(\mu_3-N)]_8$, **6-O**, contains 24 unpaired electrons (three per each U(III) center). The fact that the experimental U–E distances found for complex **6** match those calculated for **6-N** and are shorter than those computed for **6-O** suggest that $E = N$ is the experimentally characterized complex.

Conclusions

DFT and multiconfigurational quantum chemical methods were used to investigate the geometry and electronic structure of several recently synthesized polymetallic uranium nitride and azide complexes $[(C_5Me_5)U(\mu-I)_2]_3N$, **1**, $[(C_5Me_5)U(\mu-I)_2]_3O$, **2**, $[(C_5Me_5)_2U(\mu-N)U(\mu-N_3)(C_5Me_5)_2]_4$, **3**, $[(C_5Me_5)_2UN_3(\mu-N_3)]_3$, **4**, $[(C_6F_5)_3BNU(N[Me]Ph)_3]$, **5**, and $[(C_5Me_5)U(\mu_3-E)]_8$, **6**. The

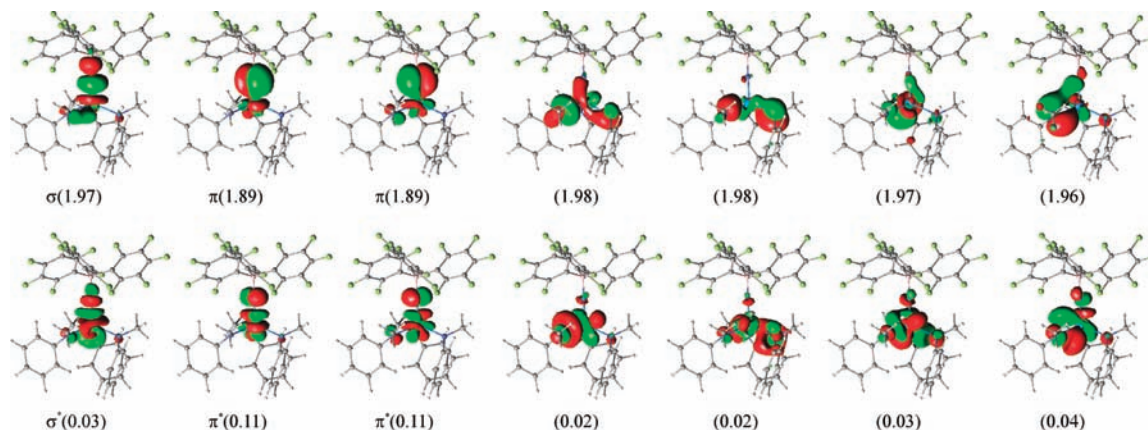


Figure 9. Natural orbitals and their occupation numbers for $(\text{C}_6\text{F}_5)_3\text{BNU}(\text{N}[\text{Me}]\text{Ar})_3$, **5**.

Table 5. Calculated U–E (E = N and O) and U–Cnt Bond Distances (Å) for $[(\text{C}_5\text{Me}_5)\text{U}(\mu_3\text{-E})]_8$ (Experimental Values Are Given for Comparison)

	E=N	E=O	experiment
U–E	2.145–2.359	2.184–2.499	2.23(2), 2.31(2), 2.32(2), 2.40(2)
U–Cnt	2.557–2.600	2.488–2.539	2.554, 2.565

calculated molecular structures are in excellent agreement with the structures determined experimentally and prove that the DFT method can be used on polymetallic complexes of a metal as heavy as uranium to obtain reliable structural predictions. Furthermore, comparison of **1** and **2** showed that differentiation of U–N vs U–O bond distances is possible. This was accomplished not only in the case of symmetrical **1**, which contained three U(IV) centers, but also in the mixed valent **2**, where one U(III) and two U(IV) centers were present. Here, we provide a theoretical proof that the complex with nitrogen is a uranium(IV) nitride, whereas its oxygen analogue is a mixed-valence uranium oxide.

The capacity to theoretically predict heavy metal–main group element bond distances is very valuable since complexes exist in which the experimental X-ray data cannot differentiate main group components like N from O in the presence of one or more metals as large as uranium. The analysis of $[(\text{C}_5\text{Me}_5)\text{U}(\mu_3\text{-E})]_8$, **6**, demonstrates that theoretical methods are indispensable when the experimental data is not definitive. Calculations indicate that both $[(\text{C}_5\text{Me}_5)\text{U}(\mu_3\text{-N})]_8$, **6-N**, and $[(\text{C}_5\text{Me}_5)\text{U}(\mu_3\text{-O})]_8$, **6-O**, are

reasonable molecules, but the experimentally determined distances for **6** match those of **6-N**.

DFT shows that the octametallic $[(\text{C}_5\text{Me}_5)_2\text{U}(\mu\text{-N})\text{U}(\mu\text{-N}_3)(\text{C}_5\text{Me}_5)_2]_4$, **3**, boat and chair conformers are very close in energy. This matches the experimental observation that both forms crystallize under the same conditions.

Finally, all polymetallic uranium complexes investigated in this work having uranium in formal oxidation state III or IV are bonded ionically with azide, nitride, or oxide. The only covalent structure is $[(\text{C}_6\text{F}_5)_3\text{BNU}(\text{N}[\text{Me}]\text{Ph})_3]$, which is a monouranium complex with uranium in formal oxidation state VI and a substantially different nature of the U–N(nitride) type of bonding from that in complexes **1**, **3**, and **4**.

Acknowledgment. For support of this project, we thank the Chemical Sciences, Geosciences, and Biosciences Division of the Office of Basic Energy Sciences of the Department of Energy under Contracts USDOE/DE-SC002183 (L.G.) and USDOE/DE-FG03-86ER13514 (W.J.E.) and the Swiss National Science Foundation (Grant No. 200020-120007). We acknowledge Joseph W. Ziller for the X-ray crystallography of $[(\text{C}_5\text{Me}_5)\text{U}(\mu_3\text{-E})]_8$.

Supporting Information Available: Cartesian coordinates of all the structures considered together with their absolute energies. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA103588W