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DOI:

[10.1039/C8CC05581E](https://doi.org/10.1039/C8CC05581E)

Document Version

Accepted author manuscript

[Link to publication record in Manchester Research Explorer](#)

Citation for published version (APA):

Atkinson, B., Hu, H-S., & Kaltsoyannis, N. (2018). Post Hartree-Fock calculations of pnictogen-uranium bonding in EUF_3 ($\text{E} = \text{N-Bi}$). *Chemical Communications*, 79, 11100–11103. <https://doi.org/10.1039/C8CC05581E>

Published in:

Chemical Communications

Citing this paper

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Cite this: DOI: 10.1039/xxxxxxxxxx

Post Hartree-Fock calculations of pnictogen-uranium bonding in EUF_3 ($\text{E} = \text{N-Bi}$)

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Received Date
Accepted Date

DOI: 10.1039/xxxxxxxxxx

www.rsc.org/journalname

NUF_3 is identified as having a $\text{N} \equiv \text{U}$ triple bond, as has been previously found (Andrews *et al.*, *Angew. Chem. Int. Ed.*, 2008, 47, 5366). By contrast, while previously reported calculations on PUF_3 and AsUF_3 (Andrews *et al.*, *Inorg. Chem.*, 2009, 48, 6594) gave a $\text{E} \equiv \text{U}$ triple bond, our calculations suggest a single bond for both molecules, with antibonding π^* and non-bonding $5f_{\text{U}}$ orbitals significantly occupied, and highly multiconfigurational wavefunctions. We propose this difference to be due to the smaller [6,6] active space used (σ , π , π^* and σ^*) in the previous studies. In our calculations, a [6,16] active space was employed in order to include uranium f-orbitals and pnictogen d-orbitals.

Uranium's central role in nuclear power necessitates a detailed knowledge of its chemistry, including at the most fundamental level. Pnictogen-actinide chemistry is an understudied area, and in addition to being of fundamental interest, an understanding of uranium-nitrogen chemistry is important for developing future applications of the actinides, such as the potential for uranium nitride to be used as a replacement for uranium oxide fuels, given its higher melting point, thermal conductivity and increased density.¹

The terminal uranium nitride molecules which have been studied spectroscopically were summarised by King and Liddle in 2013; the molecules UN , UN_2 ,² NUNH (featuring both a double and triple U-N bond)³ and NUF_3 ⁴ were all isolated in inert gas matrices, and all feature $\text{U} \equiv ^{14}\text{N}$ stretching frequencies between 938–1051 cm^{-1} .¹ The first uranium nitride molecule isolable at ambient conditions was reported by King *et al.* in 2013, featuring the highly sterically hindered polydentate $\text{Tren}^{\text{TIPS}}$ lig-

and $(\text{N}(\text{CH}_2\text{CH}_2\text{NSi}^i\text{Pr}_3)_3)$.⁵ $\text{Tren}^{\text{TIPS}}$ has subsequently been successfully employed in isolating a range of pnictogen-actinide complexes, including $\text{U}(\text{Tren}^{\text{TIPS}})(\text{PH})$ featuring a double $\text{U}=\text{P}$ bond,⁶ and the tetrameric $[\text{U}(\text{Tren}^{\text{TIPS}})(\text{AsK}_2)]_4$ featuring a $\text{U} \equiv \text{As}$ triple bonding interaction.⁷

Andrews *et al.* also reported data for PUF_3 and AsUF_3 . They obtained argon matrix isolated IR spectra of the three molecules, with U-F stretches being observed in the 520–620 cm^{-1} region. The only pnictogen-uranium stretch observed was for NUF_3 (at 938 cm^{-1}); the P-U stretch and As-U stretch were not observed but were calculated to lie outside the window of the experimental spectra. Density functional theory (DFT) calculations were performed alongside complete active space-SCF (CASSCF) calculations with second-order perturbation theory (CASPT2). A 6 electrons in 6 orbitals ([6,6]) active space was employed, which included the σ , π , π^* and σ^* orbitals of the pnictogen-uranium bond. Effective U-E bond orders were 2.78, 2.39 and 2.21 for NUF_3 , PUF_3 and AsUF_3 respectively, indicating significant multiple bonding, with a weakening of π bonding down group 15.

In this contribution, we report superior post Hartree-Fock calculations on EUF_3 ($\text{E} = \text{N-Bi}$). Calculations were performed at the CASSCF⁸ and CASPT2 levels of theory,^{9,10} but with a substantially larger active space than previously used; 6 electrons in 16 orbitals. This was chosen to include the uranium 5f, 6d and 7s valence orbitals, along with the pnictogen np valence orbitals. For NUF_3 , the principal conclusion from the present larger active space calculations is very similar to that calculated by Andrews *et al.* with a [6,6] active space, *i.e.* there is a $\text{U} \equiv \text{N}$ triple bond. A U-N bond length of 1.753 Å was calculated, *vs.* 1.759 Å from L. Andrews *et al.*. Geometric parameters are summarised in Fig. 1, and key vibrational frequencies in Table 1. The wavefunction is largely monoconfigurational with the $\sigma^2\pi^4$ configuration making up 86.6% of the wavefunction. The $^1\text{A}_1$ state was calculated to be the ground state; the first excited state, the $^3\text{A}''$ state, predominantly of $\sigma^1\pi^45f_{\text{U}}^1$ character, lies 1.60 eV higher in energy. The vast majority of the active electrons are inside the equivalent of Andrew's [6,6] active space (*i.e.* the σ and π bonding and anti-

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[†] Electronic Supplementary Information (ESI) available: computational methodology, energies and natural orbital occupancies of excited states, full vibrational frequencies and optimised geometric parameters. See DOI: 10.1039/b000000x/

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bonding orbitals) with only 0.042 electrons in the remaining 10 orbitals of the active space. This suggests that, for NUF_3 , the [6,6] active space is perfectly adequate.

Fig. 1 The ground state geometries of NUF_3 (left, C_{3v} , 1A_1), PUF_3 (middle, C_s , $^1A'$) and AsUF_3 (right, C_s , $^1A'$). Bond lengths given in ångstrom, bond angles in degrees. Blue: nitrogen, black: phosphorus, pink: arsenic, red: uranium, yellow: fluorine.

The assignment of a triple bond for NUF_3 is clear; the effective bond order $BO_{\text{eff}} = 2.73$. This is firmly supported by the U-N bond critical point (BCP) ellipticity $\varepsilon = 0.00$ (Table 2). BCP ellipticities measure the extent to which the electron density is preferentially accumulated in a given plane containing the bond path connecting two chemically bonded atoms.¹¹ Cylindrically symmetric bonds (e.g. single or triple bonds) have ellipticities (close to) zero, while double bonds feature significantly non-zero ellipticity values. The triple bond is reflected in both the calculated and observed stretching frequencies. In argon matrix IR absorption spectra, Andrews *et al.* observed the N-U stretching frequency at 938 cm^{-1} , compared to a calculated 921 cm^{-1} (at the [6,6] CASPT2 level of theory). In this work, the N-U stretching frequency is calculated to be 928 cm^{-1} (Table 1), though given that argon matrix effects are not included in the gas phase calculations, this slight improvement in the agreement may be fortuitous. Two very small imaginary frequencies are present (at $9.52i\text{ cm}^{-1}$ and $0.73i\text{ cm}^{-1}$), though these are likely artefacts of the numerical frequency calculation, as is the 1 cm^{-1} difference between the two components of the E symmetry U-F stretch.

By contrast to NUF_3 , increasing the size of the active space has a significant effect on the geometry of PUF_3 . A [6,6] active space predicts a triple bond geometry with both the methodology of Andrews *et al.*,¹³ *i.e.* an all electron basis set with a second-order DKH hamiltonian ($r(\text{P-U}) = 2.40\text{ Å}$), and that employed in this work using a relativistic ECP ($r(\text{P-U}) = 2.44\text{ Å}$). A [6,16] active space, however, finds a singly-bonded geometry, with the π bonds partially broken ($r(\text{P-U}) = 2.74\text{ Å}$). The optimised geometry of PUF_3 is shown in Fig. 1. In comparison to NUF_3 , the UF_3 motif is much flatter, with a smaller E-U-F bond angle of 105° , vs. 123° for NUF_3 . The distortion from C_{3v} is a result of the increase of a single F-U-F angle to 128° (and a corresponding decrease of the other two).

The natural orbitals of the active space are shown in Fig. 2, and the orbital occupancy of the active space is $\sigma^{1.93}\pi^{2.14}\pi^{*1.33}5f_U^{0.51}3d_P^{0.08}$, with configurations representing $\sigma^2\pi^2\pi^{*2}$ making up 30.8% of the wavefunction. The change in ground state geometry, from triply to singly bound, can be un-

Fig. 2 The natural orbitals of the active space of PUF_3 ($^1A'$, CASPT2), shown at the 0.05 isosurface value. Occupancy number given in brackets.

derstood by the significant extent to which orbitals outside of this [6,6] active space are occupied. There are 0.52 electrons occupying nonbonding $5f_U$ orbitals, and 0.07 electrons in nonbonding $3d_P$. In the [6,6] active space, these electrons must occupy either the π bonding or antibonding orbitals, or the σ antibonding orbital, favouring the triple bonded electronic structure.[‡] The effective bond order $BO_{\text{eff}} = 1.35$ suggests either a single bond or a very weak double bond. The BCP ellipticity value (Table 2) strongly suggests a single bond assignment, and this is also supported by the delocalisation index $DI(\text{U}|\text{N}) = 0.79$. The latter metric is the Quantum Theory of Atoms-in-Molecules (QTAIM) measure of bond order.¹¹ In our systems, the delocalisation indices are rather lower than the formal bond orders, though that for the U-N bond is c. 2.6 times that for the U-P.

The $^1A'$ state was found to be the ground state, however, four other states ($^3A'$, $^3A''$, $^5A'$ and $^5A''$) were found to be within 0.07 eV of the ground state. For both the triplet and quintet multiplicities, the symmetric and antisymmetric wavefunction were close in energy, suggesting a slight distortion from an E symmetry C_{3v} state. The relative energies and orbital occupancies of the electronic states are summarised in Table S4 of the supplementary information. To establish if there are low-lying states of the *same* spatial and spin symmetry as the ground state, state-

[‡] Expanding the active space from [6,6] to [6,10] yields a geometry similar to the [6,16] calculation, though contains a mixture of U $5f$ -based, 6d-based, P $3p$ -based and 4d-based orbitals, *i.e.* it is not simply U $5f$ and P $3p$ in character. This suggests an active space larger than [6,10] is required.

Table 1 Key vibrational frequencies of NUF_3 , PUF_3 and AsUF_3 (in cm^{-1}). Calculated frequencies are at the CASPT2 level of theory. Observed (obs.) frequencies, and those from the [6,6] active space are those calculated by Andrews *et al.*^{4,12}. Frequencies not observed in experimental spectra indicated by 'n.o.'.

	E-U stretch A_1/A'			U-F stretch A_1/A'			U-F stretch E/A'			U-F stretch E/A''		
	obs.	[6,16]	[6,6]	obs.	[6,16]	[6,6]	obs.	[6,16]	[6,6]	obs.	[6,16]	[6,6]
NUF_3	938	928	921	613	630	634	540	547	548	533	546	548
PUF_3	n.o.	239	404	581	592	619	536	544	560	542	530	560
AsUF_3	n.o.	194	347	581,579	594	617	536,535	547	566	536,535	528	566

averaged CASSCF (SA-CASSCF) calculations were performed at the $1A'$ CASPT2 optimised geometry. Six states were identified within 0.5 eV, all of which had a similar bonding description. The occupation numbers of the state-averaged pseudo-natural orbitals were similar for each state; the σ occupation was 1.93 across all states, the occupation of the π orbitals varied between 1.96 and 2.06, and the occupation of largely $5f_U$ character orbitals, including the π^* orbitals, varied between 1.92 and 2.02. The relative energies and occupation numbers of the pseudo-natural orbitals of the SA-CASSCF calculation are shown in Table S19 of the supplementary information.

As with NUF_3 , the frequency calculation of PUF_3 included two imaginary frequencies, though greater in magnitude at $46.1i \text{ cm}^{-1}$ and $50.1i \text{ cm}^{-1}$, likely as an artefact of the numerical frequency calculation, and/or due to the constraint to C_s symmetry. The argon matrix IR spectra obtained by Andrews *et al.* did not observe the P-U stretch, only the three U-F stretching frequencies.⁴ As such, there is no direct experimental evidence of the $\text{P}\equiv\text{U}$ triple bond. The frequency calculation of the singly-bonded geometry (at the [6,16] CASPT2 level of theory) does, however, appear to have a better fit with the observed U-F stretching frequencies, as summarised in Table 1. However, a definite geometric assignment cannot be made for the single bonded geometry based on this improvement in fit, suggesting that the U-F stretching frequencies are not enough of a fingerprint to make unambiguous assignments of other parameters in the molecule.

Like PUF_3 , a change in the description of the bonding is seen on increasing the size of the active space at the CASPT2 level of theory for AsUF_3 ; triply bonded for a [6,6] active space ($r(\text{As-U}) = 2.54 \text{ \AA}$ as calculated by Andrews *et al.*¹²) and singly bonded for a [6,16] active space CASPT2 calculation ($r(\text{As-U}) = 2.87 \text{ \AA}$). The CASPT2 global minimum was identified as a $1A'$ state, with active space orbital occupancies of $\sigma^{1.94}\pi^{2.09}\pi^{*1.33}5f_U^{0.57}4d_{As}^{0.07}$, giving an effective bond order of 1.34 (the isosurfaces of the active space natural orbitals are shown in Fig. 3). The configurations which represent $\sigma^2\pi^2\pi^{*2}$ make up 35.2% of the total wavefunction. Like PUF_3 , the σ bond is highly polarised to phosphorus, and AsUF_3 continues the trend of worsening overlap in the π bonds down group 15. The QTAIM delocalisation index $DI(U|As) = 0.76$ (versus 0.79 for phosphorus) suggests, like phosphorus, a single bond with only slight weak π bonding character, as does the ϵ (Table 2).

Similarly to PUF_3 , there are several low lying excited states of different wavefunction symmetry; $1A'$, $3A'$, $3A''$, $5A'$ and $5A''$ are all within 0.06 eV of each other. Again, for the triplet and quintet multiplicities, the A' and A'' states are near degenerate suggesting a slight distortion from a doubly degenerate C_{3v} E-

Fig. 3 The natural orbitals of the active space of AsUF_3 ($1A'$, CASPT2), shown at the 0.05 isosurface value. Occupancy number given in brackets.

symmetry state.

A CASPT2 frequency calculation on AsUF_3 resulted in a similar improvement to PUF_3 , as shown in Table 1. However, three imaginary frequencies were observed, at $84.11i \text{ cm}^{-1}$, $69.44i \text{ cm}^{-1}$ and $32.62i \text{ cm}^{-1}$, and are possibly artefacts of the numerical frequency calculation or a result of the constraint to C_s symmetry. Again, the As-U stretch was not observed by Andrews *et al.*; only U-F stretches were. And, as before, we can not make geometric assignments from this improvement in fit.

Table 2 QTAIM delocalisation indices and atomic charges of NUF_3 , PUF_3 and AsUF_3 in their CASPT2 ground state. *For $DI(U|F)$ and $q(F)$, the figures shown are averages.

	NUF_3	PUF_3	AsUF_3
$DI(E U)$	2.037	0.787	0.758
$DI(U F)^*$	0.651	0.646	0.653
$q(U)$	+3.233	+2.977	+2.963
$q(E)$	-0.875	-0.580	-0.570
$q(F)^*$	-0.786	-0.799	-0.797
$\epsilon(E-U \text{ BCP})$	0.000	0.006	0.023

Despite the change in the pnictogen-uranium bonding environment, there is little change in the uranium-fluorine bonding of NUF_3 , PUF_3 and AsUF_3 . As shown in Fig. 1, the U-F bond length increases slightly from 2.045 Å in NUF_3 to 2.052 Å for PUF_3 and 2.051 Å for AsUF_3 . As Table 2 shows, the U|F delocalisation index and atomic charge of fluorine are essentially invariant from N to As; the change in atomic charge of uranium is almost entirely due to the change in the pnictogen.

For SbUF_3 and BiUF_3 , geometry optimisations have been performed at the CASSCF level of theory. For SbUF_3 the ground state is $^5A''$, with orbital occupancies of $\sigma^{1.94}\pi^{1.99}\pi^{*1.00}5f_U^{1.00}5d_{Sb}^{0.07}$. The ground state of BiUF_3 is $^1A'$, with orbital occupancies of $\sigma^{1.94}\pi^{2.16}\pi^{*1.58}5f_U^{0.24}6d_{Bi}^{0.08}$. The singlet, triplet and quintet, A' and A'' states lie within 0.02 eV and 0.04 eV of each other for SbUF_3 and BiUF_3 respectively. The CASSCF bonding description for both of the heavier pnictogens is consistent with that for PUF_3 and AsUF_3 at both the CASSCF and CASPT2 levels. On the basis of the CASSCF and CASPT2 optimisations of AsUF_3 and PUF_3 (as shown in Tables S12, S13, S15 and S16 of the supplementary information), we would expect a small contraction in the E-U bond length of about 0.1 Å at the CASPT2 level for SbUF_3 and BiUF_3 , but the ground state bonding description would be expected to be essentially unchanged.

The calculations presented are in contrast to those recently reported by Wang *et al.* on $[\text{EFe}(\text{CO})_3]^-$ (E = N-Bi), who found $\text{E}\equiv\text{Fe}$ triple bonds in all cases.¹⁴ They performed single-point CASSCF calculations whose wavefunctions were predominantly composed of a single configuration (c. 90% for E = As-Bi), in support of their closed-shell DFT calculations. This serves to highlight the impact of the many actinide valence orbitals in influencing their chemistry.

In summary, the calculations presented here support the previously published literature in finding a $\text{U}\equiv\text{N}$ triple bond in NUF_3 . However, for PUF_3 and AsUF_3 , the crucial role of the active space in CASSCF/CASPT2 calculations is highlighted, as for both molecules the bonding description differs on change from a [6,6] active space (*i.e.* the σ , π , π^* and σ^* orbitals), to [6,16], where nonbonding uranium f-orbitals and pnictogen d-orbitals have occupancies of about 0.50 and 0.07 respectively for both PUF_3 and AsUF_3 . Both PUF_3 and AsUF_3 , at the CASPT2 level of theory, are identified as having a polarised single σ bond with an essentially entirely broken π bond. Calculations at the CASSCF level of theory for SbUF_3 and BiUF_3 paint a largely similar picture, with the same single bonded geometry being observed. The plethora of closely-spaced excited states for the heavier pnictogen systems reflects the complexity of the electronic structure and highlights the importance of multiconfigurational methods. It is important to note that the effects of spin-orbit coupling (SOC) have not been accounted for in this work. Given the closely-spaced states found, it is very likely that a SOC-CASPT2 calculation would result in a large mixing of spin-orbit free states. However, as the bonding picture in all the low-lying states identified is essentially the same, spin-orbit coupling will not materially affect the principal conclusions of this work, *i.e.* that there is a significant reduction in the U-E bond order from E = N to E = P-Bi.

We are grateful to The University of Manchester for a PhD

studentship to B.E.A., a postdoctoral fellowship to H.-S.H., and for computational resources from the University's Computational Shared Facility. We also thank the Environmental Molecular Sciences Laboratory at the Pacific Northwest National Laboratory for a grant of computer time on the CASCADE facility (Proposal Number 49254).

Conflicts of interest

There are no conflicts to declare.

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