6594 *Inorg. Chem.* **2009**, *48*, 6594–6598
DOI: 10.1021/ic9005696

Inorganic Chemistry
Article

As≡UF$_3$ Molecule with a Weak Triple Bond to Uranium

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Received March 23, 2009

After reactions of uranium atoms with NF$_3$ and PF$_3$ to form the N≡UF$_3$ and P≡UF$_3$ molecules, the analogous reaction with AsF$_3$ produced the novel terminal arsenide As≡UF$_3$. This first molecule with a uranium−arsenic bond was identified from matrix infrared spectra through comparison with spectra of the uranium nitride and phosphide species, with spectra using other metals, and with frequencies computed by density functional and multiconfigurational wave function methods. The latter calculation describes a weak triple bond to uranium in the As≡UF$_3$ molecule, which has slightly less bonding and more antibonding character than the weak triple bond in P≡UF$_3$.

Introduction

Understanding uranium chemistry is important because of the numerous far-reaching applications for his early actinide element.[1] The relatively large size and availability of 5f orbitals for bonding interactions may facilitate unique catalytic reactions.[2] Interesting complexes with metal−ligand multiple bonds including uranium nitrogen species have been prepared.[3−6] Such complexes with organoimido (U═NR) and phosphinidene (U═PR) groups[7,8] provide examples, but no arsenic derivatives are known with any order of U−As bond. In fact no compounds with U−As bonds are listed in the Cambridge Structural Database.[9] The heavier main group elements are much less inclined to form multiple bonds, and their chemistry reflects this difference.[10]

The first examples of uranium methylidene and methylidyne molecules have been prepared in our laboratory using laser-ablated uranium atoms as the reagent. These include the CH$_2$═UH$_2$, CH$_2$═UHF, CH$_2$═UF$_2$, HC≡UF$_3$, and FC≡UF$_3$ molecules.[11−14] The well-known stability of uranium fluorine bonds has made possible the straightforward synthesis of the first U≡C triple bond and simple terminal U≡N and U≡P bond containing molecules. Through the reaction of laser ablated U atoms with CHF$_3$, NF$_3$, and PF$_3$, the simple HC≡UF$_3$, N≡UF$_3$, and P≡UF$_3$ molecules have been prepared, their matrix infrared spectra has been observed, their vibrational frequencies and structure have been calculated, and the bonding has been analyzed.[14,15] The U≡N triple bond is the strongest as the more contracted 2p orbitals of N bond more effectively with U 5f orbitals than the more diffuse P 3p orbitals. This is also expected because the electronegativity difference is larger and thus the ionic contribution to the bond energy is greater in the case of N. Thus, it should be possible to prepare the first U−As bonds from the analogous reaction with AsF$_3$, but these multiple bonds will be weak. Parallel investigations show that Mo and W atoms react with AsF$_3$ upon excitation by laser ablation or UV irradiation to form stable trigonal As≡MF$_3$ terminal arsenides.[16] Here follows a report on the formation, matrix infrared spectrum, computed structure, and bonding in the As≡UF$_3$ molecule.

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Results and Discussion

Uranium atoms, generated by laser-ablation from a solid metal target (Oak Ridge National Laboratory, high purity, depleted of ^{235}U) were found to react with AsF_3 (Ozark-Mahoning, vacuum distilled from dry NaF) diluted in argon during condensation on a 4 K cesium iodide window as described previously.[12,17] After reaction, infrared spectra were recorded at 0.5 cm^{-1} resolution using a Nicolet 750 spectrometer with an Hg−Cd−Te B range detector. Samples were annealed to allow reagent diffusion and further reaction and later irradiated for 15 min periods by a mercury arc street lamp (175 W) with the globe removed using a combination of optical filters. Common absorptions in uranium experiments using different reagents were limited to trace quantities of UN_2 and UO_2.[18,19] Common absorptions in AsF_3 experiments with different metals include very weak 808 and 785 cm^{-1} bands for AsF_5 and a pair of strong bands at 699.7 and 668.4 cm^{-1} for the AsF_2 free radical.[20]

Infrared spectra in the U−F stretching region are compared in Figure 1 for U reaction products with NF_3, PF_3, and AsF_3. The only new bands unique to U and AsF_3 are the sharp features at 580.9, 578.5, 536.7, and 535.0 cm^{-1}, which increased about 30% on annealing to 20 K, increased slightly on >220 nm ultraviolet irradiation, then decreased on annealing to 30 K. These bands are very slightly shifted from analogous 581.2, 579.0, 536.2, and 534.8 cm^{-1} bands produced by the PF_3 reaction product.[15] Two weak blue satellites at 542.7 and 541.1 cm^{-1} on the AsF_3 reaction product are very much weaker than the analogous 541.7 and 539.7 cm^{-1} bands with PF_3, which supports the possibility that $(PF_3)(P{\equiv}UF_3)$ complexes may contribute to that product spectrum. Although AsF_3 is more reactive than PF_3, we detect only a trace of UF_4 from the very weak 532.4 and 530.3 cm^{-1} bands that appear in the spectrum on annealing to 20 K.[21] Recall that UF_6 was observed in the much more reactive NF_3 and U system,[15] and weak bands increased on annealing for UF_4 as well.

Our earlier investigations of Mo, W, and U reactions with PF_3 showed that insertion followed by α-F-transfer led to the formation of terminal nitride and phosphide metal(VI) species as represented by eqs 1 and 2 for uranium.[15,22] The analogous reaction for AsF_3 is straightforward.

$$U + NF_3 \rightarrow NF_2{-}UF \rightarrow NF{=}UF_2 \rightarrow NUF_3 \qquad (1)$$

$$U + PF_3 \rightarrow PF_2{-}UF \rightarrow PF{=}UF_2 \rightarrow PUF_3 \qquad (2)$$

$$U + AsF_3 \rightarrow AsF_2{-}UF \rightarrow AsF{=}UF_2 \rightarrow AsUF_3 \qquad (3)$$

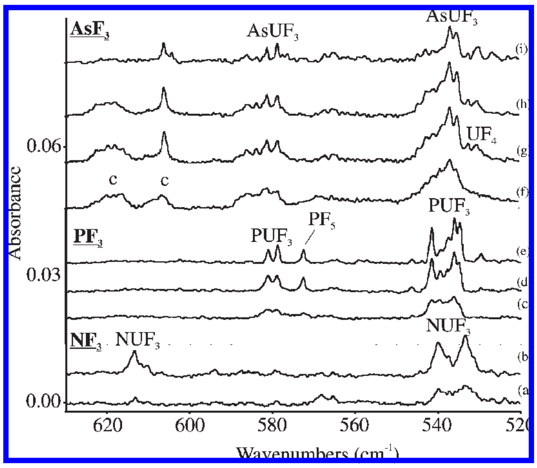

Figure 1. Infrared spectra of U atom reaction products with NF_3, PF_3, and AsF_3 in the 630−520 cm^{-1} region. (a) Spectrum after co-deposition of laser-ablated U and NF_3 at 0.3% in argon at 4 K for 60 min, (b) after 240−380 nm irradiation for 40 min, (c) spectrum after co-deposition of laser-ablated U and PF_3 at 0.4% in argon at 4 K for 60 min, (d) after >220 nm irradiation for 20 min, (e) after annealing to 20 K, (f) spectrum after co-deposition of laser-ablated U and AsF_3 at 0.5% in argon at 4 K for 60 min, (g) after annealing to 20 K, (h) after >220 nm irradiation for 20 min, and (i) after annealing to 30 K. Bands labeled "c" are common to AsF_3 experiments with other metals.

Calculations with density functional (DFT: B3LYP, BPW91)[23−27] and wave function (CASSCF/CASPT2) methods[28,29] predict the strong U−F stretching frequencies for $As{\equiv}UF_3$ to be near those for $P{\equiv}UF_3$, which are in satisfactory agreement with experimental observations (Table 1). The CASSCF predictions are higher than the B3LYP values, which are 20 cm^{-1} higher than the observed values, and the BPW91 frequencies, which are about 15 cm^{-1} higher than the observed values, which is typical for computed harmonic frequencies in comparison to observed anharmonic values.[30] Both fundamentals are apparently split approximately 2 cm^{-1} by interaction with the argon matrix. The calculation of vibrational frequencies is not an exact science, and the correlation of frequencies computed by several different methods is reassuring.

Calculations for the triplet $AsF{=}UF_2$ intermediate converged instead to a bridged $As(F){=}UF_2$ structure, which for B3LYP is 11 kcal/mol lower in energy than $As{\equiv}UF_3$ with its

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Table 1. Observed and Calculated Frequencies for the $P\equiv UF_3$ and $As\equiv UF_3$ Molecules in the Singlet Ground Electronic States with C_{3v} or C_s Structures[a]

	$P\equiv UF_3$							$As\equiv UF_3$						
approximate description	obs	cal(C)	int	cal(L)	int	cal(B)	int	obs	cal(C)	int	cal(L)	int	cal(B)	int
U−F str, a_1,a′	581.2, 579.0	619	259	608	201	595	170	580.9, 578.5	617	267	602	206	594	182
U−F str, e, a″	536.2, 534.8	560	430	558	170	552	141	536.7, 535.0	566	406	560	160	555	136
U−F str, a′				554	147	545	143				554	148	548	139
E≡U str, a′	n. o.[b]	404	26	399	22	375	12		347	34	234	3	235	3
F−U−F bend, a_1, a′		148	19	135	4	127	11		157	11	125	5	122	11
F−U−F bend, e, a″		111	12	133	16	122	3		114	12	99	8	120	3
F−U−F bend, a′				91	9	108	8				87	18	106	6
E−U-F bend, e, a″		25	54	86	12	56	14		23	40	62	7	52	9
E−U-F bend, a′				56	18	21	15				35	8	21	11

[a] Frequencies and intensities are in cm^{-1} and km/mol. Observed in an argon matrix. Frequencies and intensities computed with CASPT2 (C), B3LYP (L), or BPW91(B) methods in the harmonic approximation. Symmetry notations are first for C_{3v} from CASSCF and second for C_s from DFT. [b] Not observed because of falling below instrument limit.

stronger U−F mode computed at 545 cm^{-1} and a slightly weaker band at 528 cm^{-1} and for BPW91 this bridged structure is isoenergetic with $As\equiv UF_3$ and has a stronger U−F mode at 575 cm^{-1} and slightly weaker band at 554 cm^{-1}. Since DFT frequencies are usually above observed values,[30] the B3LYP frequencies 34 and 8 cm^{-1} below the observed are not compatible with the $As(F){=}UF_2$ assignment, and the BPW91 frequencies do not fit the observed values as well as the calculated set in Table 1. Similar calculations for $P(F){=}UF_2$ find a 16 kcal/mol lower structure with frequencies also too low using B3LYP and an 18 kcal/mol higher energy structure with frequencies too low using BPW91. However, our B3LYP calculation for the triplet $NF{=}UF_2$ intermediate converged to a stable structure 24 kcal/mol higher in energy than the $N\equiv UF_3$ molecule identified recently.[15] It appears that the hybrid density functional favors the bridged structures for the heavier main group element, which has been observed previously,[31] but the pure density functional favors the imine structures. Of most importance here, it is clear that the calculated frequencies for the bridged structures do not correlate with the observed values. The matrix cage probably makes it more difficult for such a bridged species to form, but without matrix relaxation of reaction exothermicity, gas phase reaction (eq 3) would give only the UF and AsF_2 products. Thus, matrix relaxation of the reaction energy released makes possible the stabilization of the $As\equiv UF_3$ molecule in the matrix cage.

The comparison with calculated and observed spectra for $P\equiv UF_3$ and the present new results summarized in Table 1 substantiate the formation and identification of the $As\equiv UF_3$ molecule. This is, we believe, the first molecule to be formed with a uranium−arsenic bond.

The C_{3v} symmetry structures converged by CASSCF/CASPT2 for the three $E\equiv UF_3$ molecules are illustrated in Figure 2 and parameters are given in Table 2. Notice that as the triple bond gets longer and weaker, the U−F bonds become slightly shorter. The electronic structures in all these compounds are very similar. They are characterized by ionic uranium fluorine bonds and a covalent triple bond between the metal and N, P, or As.

The $As\equiv UF_3$ molecule contains a weak triple bond to uranium with calculated 2.544 Å (CASPT2), 2.531 Å (BPW91), and 2.495 Å (B3LYP) bond lengths, slightly longer than the triple bond in $P\equiv UF_3$. Although the DFT frequencies are closer to the observed values, the structures are distorted to C_s with two equal U−F bonds and one slightly shorter U−F bond and two corresponding As−U−F angles and one larger As−U−F angle, which average to near the CASPT2 angle (Table 2). Similar distortions were found with both DFT methods for $N\equiv UF_3$ and $P\equiv UF_3$ (Table 2), but again the frequencies were predicted more closely to the observed values.[15] The DFT methods underestimate the E≡U bond lengths and overestimate the U−F bond lengths compared to CASPT2.

The active molecular orbitals that contribute to this triple bond shown in Figure 3 reveal slightly lower bonding occupancies and higher antibonding occupancies for $As\equiv UF_3$ than for $P\equiv UF_3$ (compare Figure 5 in ref 15). The natural orbital occupation numbers for the σ- and π-bonding and antibonding orbitals add to give a weak triple bond in $P\equiv UF_3$ with an effective bond order of 2.39 and a weaker triple bond in $As\equiv UF_3$ with an effective bond order of 2.21. (The effective bond order bond order (EBO) is computed as the difference between the occupation numbers of the bonding and antibonding orbitals divided by two. A fully developed single bond has an EBO close to one, while the value approaches zero as the bond dissociates.) We rationalized the strong U≡N bond as a more balanced covalent bond between contracted U 5f orbitals in the UF_3 subunit and the smaller N 2p orbitals, and the diffuse P 3p orbitals do not bond as effectively with U 5f orbitals.[15] Arsenic extends this view with the even more diffuse As 4p which bond even less effectively with U 5f orbitals and form a still weaker triple bond with the UF_3 subunit. This is also expected because the electronegativity difference is smaller, and thus the ionic contribution to the bond energy is less in the case of As.

The triple bond energies can be estimated from the energy of the main group atom, E, reaction with UF_3 to form $E\equiv UF_3$, where UF_3 has a C_s structure.[15] These CASSCF/CASPT2 calculations are approximate without ZPE or spin−orbit correction. The bond energies so calculated decrease dramatically in this series from 110 kcal/mol for U≡N to 42 kcal/mol for U≡P to 32 kcal/mol for the even weaker U≡As bond as described above.

Although terminal pnictide complexes with uranium have not been prepared, comparisons can be made to tungsten.

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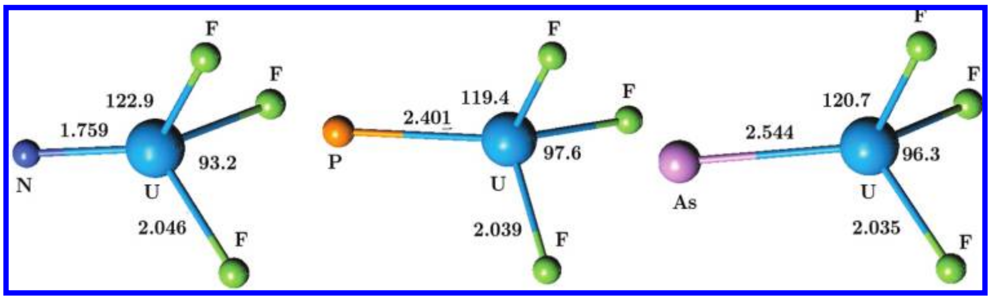

Figure 2. Structures of $\mathrm{N{\equiv}UF_3}$, $\mathrm{P{\equiv}UF_3}$, and $\mathrm{As{\equiv}UF_3}$ in C_{3v} symmetry calculated at the CASSCF/CASPT2 level of theory. Bond lengths in angstroms and angles in degrees.

Table 2. Structural Parameters Calculated for the $\mathrm{N{\equiv}UF_3}$, $\mathrm{P{\equiv}UF_3}$, and $\mathrm{As{\equiv}UF_3}$ Molecules[a]

	$\mathrm{N{\equiv}UF_3}$			$\mathrm{P{\equiv}UF_3}$			$\mathrm{As{\equiv}UF_3}$		
parameter	CAS	B3L	BPW	CAS	B3L	BPW	CAS	B3L	BPW
E≡U	1.759	1.722	1.749	2.401	2.321	2.376	2.544	2.495	2.531
U−F	2.046	2.038, 2.064	2.056, 2.064	2.039	2.040, 2.052	2.049, 2.050	2.035	2.043, 2.049	2.047, 2.048
E−U−F	122.9	109.9, 148.1	117.2, 134.5	119.7	107.0, 144.4	111.0, 136.8	120.7	104.7, 142.8	109.2, 137.5
F−U−F	93.3	98.5, 90.4	94.9, 92.1	97.6	104.1, 94.5	99.3, 96.2	96.3	104.8, 97.6	100.9, 97.2
EBO	2.78			2.39			2.21		

[a] Computed with CASPT2 (CAS), B3LYP(B3L), or BPW91(BPW) methods. Bond lengths in angstroms and angles in degrees. EBO is effective bond order as described in the text.

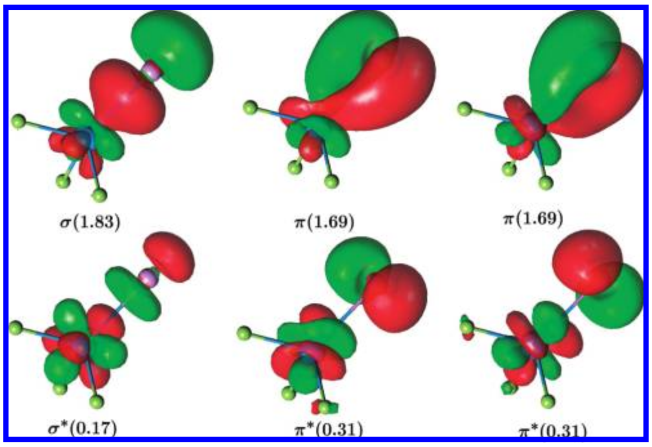

Figure 3. Active molecular orbitals in $\mathrm{As{\equiv}UF_3}$. Contour line 0.05 e/au^3. Natural orbital occupation numbers given below the orbital.

A typical W≡P bond length of 2.12 Å in organometallic complexes[32] provides a reference to show that the triple bond length computed here for uranium and phosphorus is 13% longer than the tungsten analogues. The first arsenide complex to be prepared, [$\mathrm{(N_3N)W{\equiv}As}$], revealed a W≡As bond length of 2.29 Å,[33] and our computed U≡As bond length is 11% longer. Finally, our CASPT2 U≡As bond length of 2.54 Å is 12% longer that the sum of recently tabulated triple bond covalent radii,[34] which provides further testament to our description of the uranium−arsenic triple bond as weak.

Conclusions

Like the uranium methylidyne systems,[14] macroscopic synthesis of terminal U≡N and U≡P triple bonds[15] and any U−As bonds has not yet been reported. This matrix isolation work shows that with the assistance of strongly electronegative fluorine ligands, the U(VI) oxidation state can be stabilized, and terminal triple bonds can be formed with N and reasonably well with the heavier analogues P and As. Comparison of the nitride, phosphide, and arsenide triple bonds to uranium demonstrates that U 5f orbitals bond more effectively with the smaller nitrogen ligand than with the softer phosphorus and even softer arsenic species. This is also expected because the electronegativity difference is larger, and the ionic contribution to the bond energy is greater in the case of N. The U≡As bond so formed is weak with a computed approximately 32 kcal/mol bond energy.

Theoretical Methods

After considerable success in correlating matrix spectra of small metal containing molecules with frequencies calculated by density functional theory (DFT),[11−17] similar calculations were carried out using the Gaussian 03 package,[23] the B3LYP and BPW91 density functionals,[24,25] the 6-311+G(3df) basis sets for F and As, and the small 60 electron SDD pseudopotential and basis set for uranium[26,27] to provide a consistent set of vibrational frequencies for the reaction products. Different spin states were computed to locate the ground-state product molecules. Geometries were fully relaxed during optimization, and the optimized geometry was confirmed by vibrational analysis. All of the vibrational frequencies were calculated analytically with zero-point energy included for the determination of reaction energies.

To understand the bonding involving uranium, higher level CASSCF[28] and CASPT2[29]calculations were performed for the $\mathrm{E{\equiv}UF_3}$ molecules. The basis set was of VTZP quality with the primitives obtained from the relativistic ANO-RCC basis sets: 6s5p3d1f for As, 5s4p2d1f for P, 4s3p2d1f for F and N, and 9s8p6d4f2g1h for U.[35,36] Scalar relativistic effects are included in the calculations using the Douglas−Kroll−Hess Hamiltonian as is standard in the MOLCAS software. The active space was chosen to describe the U≡E

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triple bonds: six active orbitals (three bonding and three antibonding) with six active electrons. All valence electrons plus the U 6s and 6p electrons were correlated in the CASPT2 calculations, which used the standard IPEA Hamiltonian and an imaginary shift of 0.1 to remove some weak intruder states. All calculations were performed with the MOLCAS-7 quantum chemistry software.[37] The geometries were optimized at the CASPT2 level and vibrational frequencies were computed using numerical gradients and Hessians. All calculations were performed in C_s symmetry.

Acknowledgment. We gratefully acknowledge financial support from Subgrant No. 6855694 under Prime Contract No. DE-AC02-05CH11231 to the Lawrence Berkeley National Laboratory from the DOE, and NCSA computing Grant CHE07-0004N to L.A. and from the Swedish Research Council (VR) through the Linnaeus Center of Excellence on Organizing Molecular Matter (OMM) to B.O.R. G. L. Schrobilgen and M. J. Hughes kindly provided the AsF_3 sample, and C. C. Cummins shared helpful information.

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