1 → **2** + **3** and **5** → **6**, respectively, during RNA strand cleavage. Whereas the 2′-OH group accelerates the ionic cleavage of RNA relative to DNA,[15] it slows down the radical-induced RNA strand cleavage.

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[7] Phosphite **13** was activated with pivaloyl chloride, subsequently coupled with the oligonucleotide bound to the solid phase, and the oligonucleotide synthesis was finally performed with a synthesizer.
[8] An aqueous solution (100 μL) containing the modified oligonucleotide (about 0.3 nmol) and GSH (10 – 70 nmol) was irradiated for 5 min under argon (Osram 500 W, 320 nm filter, 30 °C). The product separation was performed by HPLC on a reversed-phase column and the product analysis was done by MALDI-TOF MS. The relative ratio of the competing reaction rates k_H/k_E was determined from the ratio of products (**17** + **18**)/**19** and the glutathione concentration, see B. Giese, A. Dussy, E. Meggers, M. Petretta, U. Schwitter, *J. Am. Chem. Soc.* **1997**, *119*, 11 130.
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UF^{3+}—A Thermochemically Stable Diatomic Trication with a Covalent Bond**

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Dedicated to Professor Heinrich Nöth on the occasion of his 70th birthday

The chemistry and physics of multiply charged ions are attracting ongoing attention. One particular aspect concerns the quest for diatomic, thermochemically stable polycations. Here, thermochemical stability refers to a situation in which the polycation state AB^{n+} is lower in energy than the dissociated fragments due to charge separation, that is $A^{(n-1)+} + B^+$. Since the ionization energies (IEs)[1] of monocations AB^+ are often much larger than those of the separated neutral atoms, IE(A) and IE(B), respectively, many diatomic dications are not thermochemically stable. Nevertheless, a number of thermochemically stable, diatomic dications have recently been studied by theoretical and experimental means.[2] For diatomic trications, however, the energetic situation is even worse, because triple ionization of neutrals often requires enormous amounts of energy such that Coulomb explosion according to reaction (1) is energetically favorable.[3]

$$AB^{3+} \longrightarrow A^{2+} + B^+ \quad (1)$$

First-principle considerations predict the existence of thermochemically stable diatomic trications for rare gas (Rg) complexes of metals M for which $IE(M^{2+})$ is smaller than IE(Rg). For example, $ThHe^{3+}$ should be stable with respect to charge separation according to reaction (1), simply because $IE(Th^{2+})$ (18.3 eV) is smaller than IE(He) (24.5 eV); in fact, even the existence of $ThHe^{4+}$ has been suggested.[4] However, such highly charged rare-gas complexes offer limited conceptual insight into bonding principles because they are expected to have mostly electrostatic character.

In contrast, we are focussing on the generation of multiply charged molecules having well-defined covalent bonds in which for a diatomic trication it is the $A^{3+}-B$ bond energy which locates the AB^{n+} ground state below the $A^{(n-1)+} + B^+$ asymptote.[5] In this respect the UF^{n+} ($n = 1-3$) cations deem promising, because the combination of uranium and fluorine appears as a good candidate with respect to thermochemical stability (Table 1). Thus, the ionization energies of uranium are moderate,[6] while fluorine is the most electronegative element with a rather high IE (17.4 eV) and a pronounced

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Table 1. Ground state electronic configurations, total energies [Hartree], adiabatic and vertical ionization energies [eV] of UF^{n+} ions ($n = 1-3$) and the corresponding atomic fragments.

		Config.[a]	E_{tot}	IE_a[b]	IE_v[b]
UF^{+}[c]	quintet	$(\sigma^2\sigma^2\pi^4\sigma^1\pi^1\delta^1\phi^1)$	−575.18535	12.01	12.04
UF^{2+}[c]	quartet	$(\sigma^2\sigma^2\pi^4\pi^1\delta^1\phi^1)$	−574.74414	21.85	22.01
UF^{3+}[c]	triplet	$(\sigma^2\sigma^2\pi^4\delta^1\phi^1)$	−573.94109		
U^{+}	quartet	$(7s^2 5f^3)$	−475.31115	11.82	
U^{2+}	quintet	$(5f^4)$	−474.87671	19.08	
U^{3+}	quartet	$(5f^3)$	−474.17571	32.32	
F^{-}	singlet	$(2s^2 2p^6)$	−99.74954	3.32[d]	
F	doublet	$(2s^2 2p^5)$	−99.62761	17.27	
F^{+}	triplet	$(2s^2 2p^4)$	−98.99301		

[a] Only the occupations of the valence orbitals are given. Assuming ground states with maximal orbital momentum, these are ^5I for UF^{+}, ^4I for UF^{2+}, and ^3H for UF^{3+}. [b] Ionization into the next charge state,that is $A^{n+} \rightarrow A^{(n+1)+}$. [c] Optimized bond lengths: 1.98 Å for UF^{+}, 1.94 Å for UF^{2+} and 1.85 Å for UF^{3+}. [d] This entry corresponds to the electron affinity (EA).

tendency to form strong, significantly polarized covalent bonds to many metals.

A convenient route to generate multiply charged ions is provided by charge-stripping (CS) mass spectrometry[7] in which mass-selected precursor cations are further ionized in high-energy collision experiments. For example, charge-stripping of UF^{+} yields appreciable amounts of the UF^{2+} dication according to reaction (2), occurring in a collision with the target gas T.

$$UF^{+} + T \longrightarrow UF^{2+} + T + e \quad (2)$$

The energy balance of reaction (2) is equal to the vertical ionization energy (IE_v) of the projectile ion. To a first approximation, this quantity can be measured by the kinetic energy loss of the dication beam; this quantity is usually referred to as the Q_{min} value.[8] Accordingly, the energy-resolved CS spectrum of UF^{+} gives $Q_{min} \approx IE_v(UF^{+}) = 11.8 \pm 0.5$ eV. This result agrees quite nicely with the theoretically predicted value of $IE_v(UF^{+}) = 12.04$ eV (Table 1). Using the almost negligible difference between the vertical and adiabatic ionization energies (IE_a), together with complementary thermochemical information,[1] we conclude that UF^{2+} has a dissociation energy $D(U^{2+}--F) = 6.5$ eV and is stable towards Coulomb explosion into U^{+} and F^{+} by as much as 12.0 eV. Thus, not unexpectedly UF^{2+} adds to the series of thermochemically stable diatomic dications among the binary element fluorides.[2]

In the same manner, UF^{3+} is accessible by subjecting mass-selected UF^{2+} to a CS experiment according to reaction (3). In

$$UF^{2+} + T \longrightarrow UF^{3+} + T + e \quad (3)$$

addition, UF^{3+} formed by electron ionization of gaseous UF_6 in the ion source was subjected to a charge-exchange (CE) experiment in which the trication is collided with a target gas to afford mono- and dications, respectively. Along with U–F bond cleavage to afford the U^{3+} fragment, the CE mass spectrum of mass-selected UF^{3+} (m/z 85.7) displays signals at m/z 126.5 and 257, respectively (Figure 1). In conjunction with the fragmentation pattern, these signals unambiguously confirm the identity of UF^{3+} as a genuine diatomic trication.

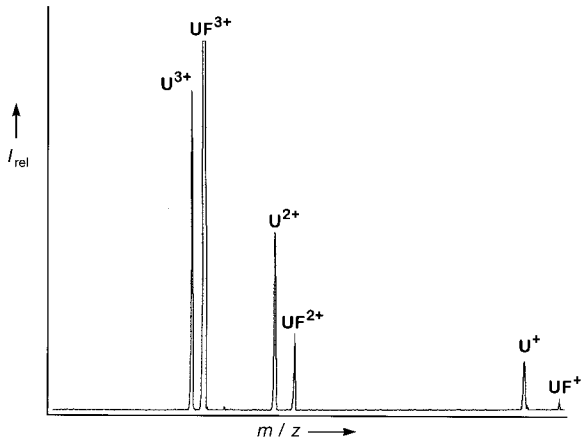

Figure 1. Charge-exchange mass spectrum of mass-selected UF^{3+} using neon as collision gas. In addition to fragmentation of the trication to afford $U^{3+} + F$, significant peaks due to the dicationic species U^{2+} and UF^{2+} as well as the corresponding monocations U^{+} and UF^{+} are observed. Note that the precursor UF^{3+} beam is off-scale (cut off at about 10 % intensity).

Further, $Q_{min}(UF^{3+})$ is determined as 22.7 ± 1.0 eV by energy-resolved charge stripping.[9] Assuming that $Q_{min} \approx IE_v$, this experimental number is again in good agreement with the calculated values of $IE_v(UF^{2+}) = 22.01$ eV and $IE_a(UF^{2+}) = 21.85$ eV, respectively (Table 1).

The key issue is the thermochemical stability of UF^{3+} trication. To our surprise, the higher ionization energies of the uranium atom are ill-defined. Thus, a recent compilation of Liu et al.[6] quotes several experimental values for $IE(U^{+})$ such as 11.07, 11.45, and 11.59 eV, while for $IE(U^{2+})$ the discrepancy between the experimental values is even larger, that is 17.73, 17.92, and 19.8 eV. In their detailed theoretical study, Liu et al. predict $IE(U^{+}) = 12.00$ eV and $IE(U^{2+}) = 18.62$ eV at the ACPF level of theory. Our less sophisticated CCSD(T) approach yields $IE(U^{+}) = 11.82$ eV and $IE(U^{2+}) = 19.08$ eV which is in acceptable agreement with the ACPF results. It appears premature, however, to adopt either of these values uncritically, because the spread of the experimental data is most likely due to systematic rather than statistical errors, and the computational approaches do not explicitly consider the appreciable spin-orbit coupling of uranium, but rather treat it in a state-averaged manner. As far as our calculations of UF^{n+} are concerned a further complication arises from the fact that the four uncoupled electrons in UF^{+}, three in UF^{2+}, and two in UF^{3+} give rise to a vast manifold of low-lying electronic states with different occupations of the more or less nonbonding 5f orbitals. For the time being, we will not dwell on these aspects any further and shall simply rely on the theoretical data due to the reasonable agreement of the calculated and measured ionization energies for UF^{n+} ($n = 1, 2$).

Accordingly, not only UF^{2+}, but also UF^{3+} is predicted to be a thermochemically stable polycation with $D(U^{3+}-F) = 3.7$ eV and $D(U^{2+}--F^{+}) = 1.9$ eV, respectively (Figure 2). Hence, it is the favorable U – – F interaction which brings the trication below the asymptote for Coulomb explosion to yield U^{2+} F^{+}, that is the covalent bonding in the trication compensates for $IE(U^{2+}) > IE(F)$. Asides this mere energetic

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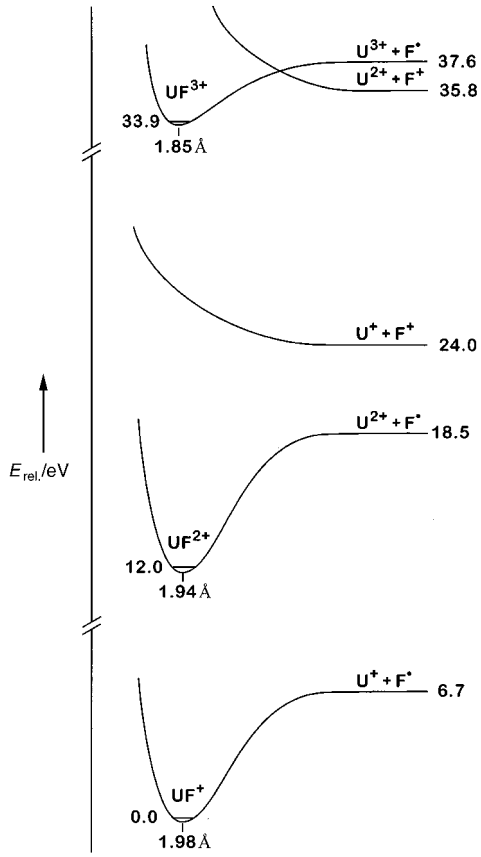

Figure 2. Schematic energy diagram for UF^{n+} ions ($n = 1-3$) and the associated dissociation asymptotes. Note that the energy axis (in eV) is not proportional.

analysis, covalent bonding in the trication is also implied by the formal charge on uranium which amounts to 3.4 in the trication as compared to 2.6 in the di- and 1.6 in the monocation, respectively. Thus, even in UF^{3+} trication, fluorine acts as a strongly electron-withdrawing ligand which further increases the charge on uranium.

Finally, let us address an apparent discrepancy of the calculated and experimental thermochemistry of UF^{n+} ($n = 1-3$). Thus, for the monocation our calculations predict $D(U^+-F) = 6.7$ eV, while a value of 4.9 ± 0.5 eV has been derived in an early guided-ion beam study from the threshold of about 1.4 eV associated with reaction (4).[10]

$$U^+ + SiF_4 \longrightarrow UF^+ + SiF_3 \qquad (4)$$

Although the experimental approach used in this earlier study was not that advanced as nowadays,[11] we will not doubt the threshold measurement in itself. However, recent experimental and theoretical studies indicate that formal F-atom transfer to a metal cation is associated with a considerable barrier due to the electron-transfer harpoon-like mechanism involved.[12, 13] Thus, the experimental value derived from reaction (4) may better be regarded as a lower limit for $D(U^+-F)$ which is consistent with the caluclated figure.

In conclusion, UF^{3+} is predicted as the first diatomic trication whose thermochemical stability is due to covalent bonding in the triply charged state. Nevertheless, this deduction relies on the computed ionization energies of uranium. Hence, a more accurate experimental evaluation of these fundamental quantities is very much indicated. In turn, future theoretical approaches need to explicitly incorporate spin-orbit effects for an accurate energetic description of coordinatively unsaturated uranium compounds such as UF^{n+} ($n = 1-3$).

Experimental and Computational Procedures

The experiments were performed with a modified VG ZAB/HF/AMD 604 four-sector mass spectrometer of BEBE configuration (B stands for magnetic and E for electric sectors), which has been described elsewhere.[14] UF^{n+} ions ($n = 1-3$) were generated by electron ionization (electron energy 50–100 eV) of gaseous UF_6. After acceleration by a 8 kV voltage, the ions of interest were mass-selected using B(1)E(1) at a mass resolution of $m/\Delta m \approx 4000$. The charge-stripping experiments[15] of monocations were performed by colliding the ions with oxygen (50–80 % transmission, T); for charge stripping of dications, helium and neon were used as collision gases.[5] Q_{min} values were determined by energy scans with E(1) for B(1) mass-selected species at energy resolutions of $E/\Delta E \approx 6000$. As references for the calibration of the energy scale, we applied the commonly used toluene standard[8] assuming $Q_{min} = 15.7$ eV for the transition $C_7H_8^+ \rightarrow C_7H_8^{2+}$. Due to hardware limitations of the A/D interface, the Q_{min} values were acquired as single-scans with an *x*/*y* recorder in order to achieve maximal energy resolution; indications for the presence of electronically excited precursor ions were not observed in the charge-stripping experiments.[15, 16] The other spectra were accumulated and on-line processed with the AMD/Intectra data system; five to 50 spectra were averaged to improve the signal-to-noise ratio.

Within the scope of a conceptual description of UF^{n+} ($n = 1-3$), a complete coverage of all possible states at a highly correlated level is simply too demanding. As a compromise, we have determined the low-lying electronic states using the ADF program package[17] at the non-local spin density level (VWN exchange-correlation functional with Becke88/Perdew86 gradient corrections). A first-order treatment of relativity was achieved by inclusion of scalar relativistic effects by means of a Pauli–Hamiltonian. The inner 78 electrons ([Xe] $5d^{10}$ $4f^{14}$) of uranium and the two 1s electrons of fluorine were treated with the frozen-core approximation, while triple-ζ basis sets were used for the remaining valence electrons. Each configuration arising from distribution of the uncoupled electrons into the nonbonding 5f orbitals has been examined, and the U–F distances were optimized separately. This procedure leads to a manifold of low-lying configurations, e.g. 22 quintet and triplet states of UF^+ within 2 eV. Then, the lowest roots (< 0.35 eV) were examined further using the restricted open-shell coupled cluster method CCSD(T) as implemented in MOLPRO 96.[18] For each species, the minimum geometry was re-optimized. In these calculations, we employed the quasi-relativistic effective 60-core electron pseudo potential and the associated (12s11p10d8f)/[8s7p6d4f] valence basis set by Küchle et al.[19] which was augmented by two g-type polarization functions (exponents: 1.2649 and 0.5060).[20] For fluorine, the aug-cc-pVTZ basis set was used.[21] Except for the 1s electrons of fluorine, the 5s, 5p, and 5d electrons of uranium, all valence electrons were correlated in the calculations.

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Rational Synthesis of Stable Channel-Like Cavities with Methane Gas Adsorption Properties: [{$Cu_2(pzdc)_2(L)$}$_n$] (pzdc = pyrazine-2,3-dicarboxylate; L = a Pillar Ligand)**

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The synthesis and characterization of coordination networks with channel structures that provide new sizes, shapes, and chemical environments are of great current interest.[1–5] This is not only because of their intriguing structural diversity, but also because of their potential for applications in molecular adsorption, ion exchange, and heterogeneous catalysis.[2, 6–10] However, the synthesis of such functional porous networks is often unsuccessful, because of the formation of an interpenetrating structure, which provides only small-sized channels or none at all.[1, 11–17] Another reason could be the deformation of the channel structure on the removal of the included guest molecules.

Although several porous structures have been reported, the methods for synthesizing stable porous networks are still in their infancy. Some successful examples of multidimensional networks that have been synthesized and structurally characterized to date are: [{$M_2(4,4'\text{-bpy})_3(NO_3)_4$}$_n$] (M = Co, Ni, Zn; 4,4′-bpy = 4,4′-bipyridine),[18] [{$Ag(teb)(CF_3SO_3)$}$_n$] (teb = 1,3,5-tris(3-ethynylbenzonitrile)benzene),[19] [{$Zn_2(btc)(NO_3)\cdot(H_2O)(C_2H_5OH)_5$}$_n$] (btc = 1,3,5-benzenetricarboxylate),[1] and [{$Zn_3(bdc)_3\cdot 2\,CH_3OH$}$_n$] (bdc = 1,4-benzenedicarboxylate).[20]

It has been demonstrated that the pillared-layer structure is effective for the construction of three-dimensional networks with large channels.[21] Although this type of network has been investigated in the hydrogen-bonded assembly of organic molecules, the organic pillared-layer structures obtained are unstable in the absence of included guest molecules.[21, 22] In comparison, coordination networks give more stable struc-

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