borhood of equilibrium, e.g. phase transitions, can however be formally described in a similar way mathematically; see H. Haken, A. Wunderlin: *Die Selbststrukturierung der Materie*, Vieweg, Braunschweig 1991. In our view microscopic structure formation (self-organization) under the influence of a primarily formed matrix (as in the case of 3[3]) and such that proceed via weak interactions with an external matrix have probably had importance in prebiotic elementary processes (formation of biopolymers) (cf. also the definitions "matrix" and "template" in O.-A. Neumüller: *Römpps Chemie-Lexikon*, Franckh'sche Verlagshandlung, Stuttgart 1985 and 1988, p. 2510 and 4152, respectively).

- [14] A further future aspect emerges from the fact that in **1** and **2** not all positions in the two equivalent layers neighboring the polar $\{V_3O_7\}$ units are occupied, so that other units can also be encapsulated in the cluster shells. For example, in the cluster shell of **2** also a disordered NO_3^- ion can occur with one NO moiety replacing the N(N)N one: A. Müller, R. Rohlfing, unpublished results.

Synthesis and Structure of the First Tellurium(III) Radical Cation**

By Már Björgvinsson, Thorsten Heinze, Herbert W. Roesky,*
Frank Pauer, Dietmar Stalke, and George M. Sheldrick*

Dedicated to Professor Karl Heinz Büchel
on the occasion of his 60th birthday

Although compounds with tellurium–nitrogen bonds have been used for some time in organic synthesis,^[1] it is only in the last few years that they have been unambiguously structurally characterized.^[2–12] Our interest in Te–N compounds was particularly stimulated by the isolation of the novel tricyclic tellurium nitride $(ClTeNSN)_3N \cdot 3 DMF$.^[10] In general, however, suitable stable precursors for the preparation of new Te–N compounds have been lacking. Recently, we prepared $Te(N(SiMe_3)_2)_2$ (**1**) in relatively good yields.^[12] In our study of the coordination properties of **1** toward silver cations, we have isolated and structurally characterized the AsF_6^- salt of the first Te^{III} radical cation, $[Te(N(SiMe_3)_2)_2]^+$ (**2⁺**).

A dark blue solution of **3** was formed when a cold mixture (–78 °C) of **1** and $Ag^+AsF_6^-$ in CH_2Cl_2 was allowed to

warm to room temperature [Eq. (a)]. Large crystalline blocks of **3** were isolated and its crystal structure was determined by low-temperature X-ray crystallography.^[13] The crystals of **3** consist of monomer **2⁺** coordinated by two AsF_6^- anions; thus, chains of alternating cations and anions are formed (Fig. 1).

The average Te–N distance of **2⁺** (196.6(4) pm) is 8 pm shorter than that of its neutral analogue **1**,^[12] indicating some multiple-bond character. Furthermore, the Si–N distances are longer, the average Si–N–Te bond angle is larger, the average Si–N–Si bond angle is smaller, and the pyramid formed from the N, Si, Si, and Te atoms is flatter than in **1**. These findings correlate well with the model of enhanced

back-bonding of nitrogen-atom lone pairs to the positively charged tellurium atom of **2⁺**. Two long interionic Te...F contacts (318.6(1) (F 2) and 317.9(1) (F 6) pm), shorter than the van der Waals distance (355 pm^[14] and 353 pm^[15]) are present in **3** (Fig. 1).

Fig. 1. Molecular structure of **2⁺** and its nearest AsF_6^- neighbors (hydrogen atoms have been omitted). Broken lines show relatively short interionic contacts. Important distances [pm], bond angles [°], and torsional angles [°] for **2⁺**: Te 1–N 1 196.4(4), Te 1–N 2 196.8(4), N 1–Si 1 179.5(4), N 1–Si 2 180.0(4), N 2–Si 3 179.4(4), N 2–Si 4 179.2(4); N 1–Te 1–N 2 106.8(1), Te 1–N 1–Si 1 123.4(2), Te 1–N 1–Si 2 114.6(2), Te 1–N 2–Si 3 114.2(2), Te 1–N 2–Si 4 122.5(2), Si 1–N 1–Si 2 120.7(2), Si 3–N 2–Si 4 121.3(2); N 2–Te 1–N 1–Si 1 51.7, N 2–Te 1–N 1–Si 2 –141.0, N 1–Te 1–N 2–Si 3 –139.3, N 1–Te 1–N 2–Si 4 56.3. For the AsF_6^- ion the bond distances and bond angles lie in the following ranges: As–F 165.9(5) – 169.8(4) pm, F–As–F 87.2(4) – 91.5(5)°, respectively. The fluorine atoms are disordered in the As–F 1–F 2–F 3–F 4 plane [13].

The solution ¹H NMR spectrum of **3** gave a relatively broad signal ($\Delta\nu_{1/2} = 18$ Hz), as expected for a radical. Only a single broad peak ($\Delta\omega_{1/2} \approx 15$ G) was observed in the ESR spectrum of **3** in $CDCl_3$, indicating a small spin density on the nitrogen atoms. Similar behavior has been observed for the isovalent pnictogen analogues of **2⁺**, $[P(N(SiMe_3)_2)_2]^+$ (**4⁺**) and $[As(N(SiMe_3)_2)_2]^+$ (**5⁺**).^[16] It was further evident from the hyperfine coupling constants of **4⁺** and **5⁺** that the single electron was localized in a p orbital on the pnictogen atoms. Similar behavior is expected for **2⁺**. Thus, assuming an AX_2E_2 electron-pair arrangement around tellurium in **1**,^[17] removal of an electron from **1** would result in a rehybridization of the tellurium atom such that a pair of electrons are in a sp^2 orbital and the single electron is in a p orbital.^[18]

Scheme 1. Rehybridization of the tellurium orbitals on conversion of **1** to **2⁺**.

The bulky $N(SiMe_3)_2$ groups are expected to hinder the dimerization of **2⁺**. Furthermore, **2⁺** is stabilized by the interionic $2^+ \cdots AsF_6^-$ contacts. By contrast, dimers with relatively short Te...Te contact distances are present in the crystals of the neutral compound **1**.^[12] Dimerization of **2⁺** is probably hindered owing to steric factors, which would reduce the energetically favorable ion-pair contacts, and electrostatic repulsion between the positively charged telluri-

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um atoms. Contact ion pairs are presumably also present in CH_2Cl_2 and CHCl_3 solvents since no sharp ^{19}F NMR resonances were observed in freshly prepared solutions of **3**. Concentrated solutions of **3** are only metastable at room temperature, however, their blue color disappearing after approximately one week.

The isolation of a Te^{III} radical cation and the determination of its detailed geometry affords a unique opportunity for a general study of the nature of related species. Furthermore, the unexpected oxidation of **1** by $\text{Ag}^+ \text{AsF}_6^-$ strongly suggests that this synthetic method could be generalized to other tellurium compounds.

Experimental Procedure

All manipulations were performed under an inert atmosphere of dry nitrogen gas inside a drybox or on a glass vacuum line. The CH_2Cl_2 and CHCl_3 solvents were dried over P_2O_{10} and distilled and stored over molecular sieves (4 Å) prior to use. In a typical preparation, **1** (1.13 g, 2.51 mmol) and $\text{Ag}^+ \text{AsF}_6^-$ (0.74 g, 2.50 mmol) were loaded into separate arms of an H-shaped glass reaction vessel (equipped with teflon valves and a glass frit). After dissolving the compounds in CH_2Cl_2 (30 ml) the solutions were thoroughly mixed at -78°C and the yellow solution allowed to warm to room temperature. The resulting dark blue solution was then filtered from the white-grey silver metal powder and the solvent slowly condensed off to give large black crystalline blocks of **3**. ^1H NMR (80 MHz, CDCl_3 , -50°C , ext. TMS): $\delta = 0.45$ ($\Delta\nu_{1/2} = 18$ Hz). ESR (CDCl_3 , 10°C): $g = 2.0$ ($\Delta\omega_{1/2} = 15$ G). UV/VIS (CH_2Cl_2): λ_{max} [nm] = 615.

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1, 130497-87-9; **3**, 137300-30-2; $\text{Ag}^+ \text{AsF}_6^-$, 12005-82-2.

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- [18] As pointed out by one of the reviewers, an alternative rationalization would be that an electron is removed from a doubly occupied tellurium nonbonding p orbital (b_2), perpendicular to the TeN_2 plane. This model is analogous to the MO description of the oxygen-atom lone pair in H_2O . However, for a criticism of this description see [17b], p. 32.

Tetrakis(dimethylamino)ethene: An Extremely Electron-Rich Molecule with Unusual Structure both in the Crystal and in the Gas Phase**

By Hans Bock,* Horst Borrmann, Zdenek Havlas, Heinz Oberhammer,* Klaus Ruppert, and Arndt Simon*

Dedicated to Hans Georg von Schnering on the occasion of his 60th birthday

Which organic molecules possess such low first ionization energies that they approach those of the alkaline-metal atoms Li (5.40 eV) and Na (5.14 eV)? Only a few answers can be given to this question and one of them is tetrakis(dimethylamino)ethene ($IE_1^V = 6.13$ eV^[1, a, b]). On dissolving in oxygen-free water, therefore, it forms a radical cation, presumably according to $M_{\text{solv.}} + H_{\text{solv.}}^+ \rightarrow 1/2 H_2 + M_{\text{solv.}}^{\oplus}$ with H_2 evolution.^[1c] Two-electron oxidation^[1d] by halogens (X_2) yields the dication salt, the structure of which is characterized by a central CC single bond of 150 pm length and two cyanine-like molecular halves twisted relative to each other by up to 76° ^[1e] [Eq. (a)].

The electron richness of the readily oxidizable title compound^[1f] is further illustrated by a comparison with the valence-isoelectronic hydrocarbon derivative, the tetraanion of tetraisopropylethene, $((\text{H}_3\text{C})_2\text{C}^-)_2\text{C}=\text{C}(\text{C}^-(\text{CH}_3)_2)_2$, taking into consideration the different effective nuclear charges

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