Tellurium Clusters

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The Electrochemical Synthesis of Polycationic Clusters

*Christopher Schulz, Jörg Daniels, Thomas Bredow, and Johannes Beck**

Abstract: *As a new method for the synthesis of chalcogen polycationic clusters, the electrochemical dissolution of elemental tellurium in ionic liquids (IL) or in liquid* SO_2 *is presented. ILs used are ethylmethylimidazolium triflate* $[OTf]^-$ *and tetraalkylammonium triflylimide* $[NTf_2]^-$*. Tristriflylmethanide* $[CTf_3]^-$ *was used as* $[BuMeIm][CTf_3]$ *as the electrolyte in* SO_2*. This allowed for the isolation of* $[Te_4][CTf_3]_2$*,* $[Te_6][OTf]_4$*, and* $[Te_8][NTf_2]_2$ *containing the square* $[Te_4]^{2+}$*, the prismatic* $[Te_6]^{4+}$*, and the novel barrelane-shaped* $[Te_8]^{2+}$*. The compounds are novel compositions as they do not contain the usual halometalate anions, but rather common weakly coordinating anions. The* ^{125}Te *NMR spectrum of an IL solution containing* $[Te_8]^{2+}$ *features only one broad signal at 2700 ppm. DFT calculations show that slight concerted displacements within the* $[Te_8]^{2+}$ *cluster lead to a fluxional molecular structure and a fast valence isomerism with a very low activation barrier of about 8 kJ mol*$^{-1}$*.*

Cationic clusters of main-group elements have been known for more than 200 years since the formation of deep red colored solutions in reactions of elemental tellurium with fuming sulfuric acid was observed by Klaproth. It took, however, more than 160 years until the nature of the colored species could be elucidated.[1] During the last decades, a large number of polycationic clusters of main-group elements have been synthesized in different ways and characterized structurally and spectroscopically.[2] The most applied synthetic procedure to obtain polycationic clusters implies the oxidation of the respective element with one- or two-electron oxidants like AsF_5, SbF_5, or $MoOCl_4$ or the use of a higher halide of the main-group element in presence of strong halide acceptors such as $AlCl_3$. Consequently, halometalates such as $[AsF_6]^-$, $[SbF_6]^-$, and $[AlCl_4]^-$ are the most abundant anions. For their stabilization, the reactive and highly electrophilic cationic clusters demand weakly basic and weakly coordinating anions (WCAs). Deriving from very strong Lewis acidic metal halides, the corresponding halometalates are very weakly basic and thus suitable to act as counterions. The synthetic routes involve reactions in polar solvents like liquid sulfur dioxide or hydrogen fluoride, Lewis acidic melts, and recently ionic liquids (IL).[1,3] ILs expand the synthetic possibilities owing to low reaction temperatures and their high polarity.[3] This allowed the isolation of the first superconducting polycation containing compound $[Te_4][Bi_{0.74}Cl_4]$[4] or extended nets of cations as present in $[Te_8]_2[Ta_4O_4Cl_{16}]$.[5]

Weakly coordinating anions besides the halometalates have been in the focus of research for some years.[6] Trifluoromethanesulfonate (triflate, $[OTf]^-$), bis(trifluoromethanesulfonyl)imide (triflimide, $[NTf_2]^-$), tris(trifluoromethanesulfonyl)methanide (tristriflylmethanide, $[CTf_3]^-$), tetrakis(pentafluorophenyl)borate $[B(Ph^F)_4]^-$, or tetrakis(perfluoro-*tert*-butoxido)aluminate ($[Al(OtBu^F)_4]^-$) are in widespread use in technical processes and catalytic applications. The last two mentioned coordinate even more weakly than all aforementioned ions and all of them are stable towards hydrolysis, which is a great advantage with respect to the rather sensitive halometalates. Only a few reports have been found concerning cationic clusters stabilized by anions of this type. Oxidation of tellurium by bis(fluorosulfuryl)peroxide $S_2O_6F_2$ allowed for the isolation of the fluorosulfonate $[Te_4][SO_3F]_2$.[7] $[Se_{10}][SO_3F]_2$ is the product of the reaction of $[Se_{10}][AsF_6]_2$ with SO_3 under liberation of AsF_5, and the hydrogendisulfate $[Se_4][HS_2O_7]_2$ was obtained by dissolution of selenium in oleum with SO_3 acting as the oxidizing agent.[8,9]

The synthesis of main-group element polyanions by electrochemical reduction is known since more than a century.[10] Kraus observed the reductive dissolution of metallic Pb in liquid ammonia[11] and Zintl identified the $[Pb_9]^{4-}$ polyanion by dissolution of a lead cathode in a solution of NaI in NH_3.[12] The reductive cathodic dissolution of metal telluride electrodes in ethylenediamine has already proven to be a suitable synthetic route to polyanionic clusters and expanded anion structures by the work of Warren, Haushalter, and Bocarsly.[13]

We expanded the synthetic methods to the electrochemical oxidation of elemental chalcogens. Among the chalcogen group, tellurium has shown to have the largest tendency to form positively charged clusters. Thus we focused our experimental work on this element. We found the anodic dissolution of elemental tellurium in ionic liquids to be an appropriate method, which is now applied for the first time to synthesize polycationic clusters stabilized by common weakly coordinating anions. Ionic liquids have proven to be suitable solvents for manifold electrochemical processes.[14]

Experiments were carried out in H-shaped cells with a glass frit between the two compartments and Teflon screw valves. The cells were modified for electrolytic reactions by stiff steel wires passing through the axes of the valves. Rods of tellurium and of carbon were used as electrodes. These were fixed at the wires and immersed in diverse ILs as electrolytes, consisting of substituted imidazolium or tetraalkylammonium cations and the aforementioned WCAs (Supporting Informa-

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tion, Figure S1). During many attempts with various ILs we found that those ILs based on trifluoromethanesulfonyl anions are the most suitable ones. Since chalcogen polycations are highly sensitive to moisture, the designated ILs have to be anhydrous. To achieve this, we avoided the effort to dry commercial ILs but instead synthesized the ILs by a non-aqueous synthetic route in analogy to the preparations described for [BuMeIm][BF_4] and [BuMeIm][PF_6].[15] From equimolar amounts of anhydrous [EtMeIm]Cl or [NBu_3Me]Cl and Na[OTf] or Li[NTf_2] in absolute dichloromethane,[16] the alkali metal chloride precipitates yielding the respective IL in suitable quality after evaporation of CH_2Cl_2 as a light yellow oil. For the IL [BuMeIm][CTf_3],[17] this procedure was applied starting from Cs[CTf_3] (synthesized from MeMgCl and CF_3SO_2F in THF and subsequent precipitation with CsCl[18]) and [BuMeIm]Cl.

Each of the different ILs afforded slightly different experimental conditions for a successful cluster synthesis. An electric current with a constant voltage of 4 V was applied to the cell filled with [EtMeIm][OTf]. Within three weeks, the anodic solution turned deep red–violet. Liquid sulfur dioxide was condensed onto the solution, which caused the precipitation of deep brown block-shaped crystals of [Te_6][$OTf]_4$. By repeated washing with sulfur dioxide within the vessel, a deeply brown crystalline powder of [Te_6][$OTf]_4$ was obtained, which was almost phase-pure according to the X-ray powder diffractogram (XRD; Supporting Information, Figure S7). With [NBu_3Me][NTf_2], a constant voltage of 6 V was applied and the cell was heated to +50 °C using an oil bath. The elevated temperature turned out as essential. The high viscosity of this IL at ambient temperature limited the cell current. In a typical experiment, the current increased from 20 μA at +20 °C on heating to 250 μA. After two weeks, CH_2Cl_2 was slowly condensed into the deep red–violet anodic solution. On decreasing the polarity, deep purple, needle-shaped crystals of [Te_8][$NTf_2]_2$ precipitated. Attempts to isolate neat [Te_8][$NTf_2]_2$ resulted in complete blackening of the powder. According to XRD, elemental tellurium had been formed, very probably generated by a disproportionation reaction of the polycation. The greater stability of [Te_6][$OTf]_4$ compared to [Te_8][$NTf_2]_2$ is possibly based on the lower dielectricity constants of NTf_2-based ILs compared with OTf-based ILs.[19] [BuMeIm][CTf_3] was used in the electrolysis as the conducting salt in a dilute solution of liquid sulfur dioxide. After an entire reaction time of one week at a constant voltage of 6 V, the tellurium anode was sufficiently dissolved to give a deep red solution. Upon concentration by slow evaporation of SO_2 at room temperature red, plate-shaped crystals of [Te_4][$CTf_3]_2$ were obtained. During the electrolysis, the catholytes attained a dark color and the carbon electrodes decomposed by swelling and exfoliation. The reactions at the cathode were not examined but probably the cations of the electrolytes are discharged to radicals, which decompose under reaction with the carbon electrode.

All three polycation-containing compounds were characterized by crystal structure analyses. [Te_4][$CTf_3]_2$ contains the well-known square $[Te_4]^{2+}$ cluster as previously reported in numerous compounds, for example, as the $[AlCl_4]^-$,[20] the $[SbF_6]^-$[21] or the $[HfCl_6]^{2-}$[22] salt. The Te–Te bonds of 2.670 and 2.667 Å are in the normal range; the angles of 87.91° and 92.09°, however, deviate from square symmetry and indicate the deformation to a rhombus. This originates from interactions between $[Te_4]^{2+}$ and oxygen atoms of surrounding $[CTf_3]^-$ anions (Supporting Information, Figure S4). Despite all trifluoromethanesulfonyl anions belonging to the class of weakly coordinating anions, the high electrophilicy of the naked cationic clusters leads to donor–acceptor interactions between anions and cations. The methanide anions are not significantly affected by this coordination and show bond lengths and angles in line with the respective potassium salt.[23]

[Te_6][$OTf]_4$ contains the trigonal-prismatic $[Te_6]^{4+}$ cluster, as previously reported for [Te_6][$AsF_6]_4$·2 SO_2, [Te_6][$AsF_6]_4$ < M. < 2 AsF_3[24], [Te_6][Se_8][$AsF_6]_6$·SO_2,[25] and [Te_6][$AsF_6]_4$·1.5 $(CN)_2$.[26] However, the triflate salt is the first example of this cation with crystals not containing any solvent. The structure of the tellurium cluster is almost identical to the ones in the aforementioned compounds. With bond lengths from 2.692 to 2.724 Å within the triangular faces and 3.061 to 3.135 Å along the prism edges the cluster represents an almost undistorted trigonal prism. The triflate anions do not show any notable differences when compared to the respective alkali metal salts.[27]

Electrolytical dissolution of elemental tellurium in the IL [NBu_3Me][NTf_2] gives the novel eight-atomic cluster ion $[Te_8]^{2+}$, representing a further isomer among the octatellurium dications (Figure 1). The $[Te_8]^{2+}$ cluster adopts the barrelane structure, named after the bicyclo[2.2.2]octane, C_8H_{14}.[28] This structure motif is also present as the heteropolycation $[Te_2Se_6]^{2+}$ in the structure of [Te_2Se_6][Te_2Se_8]-

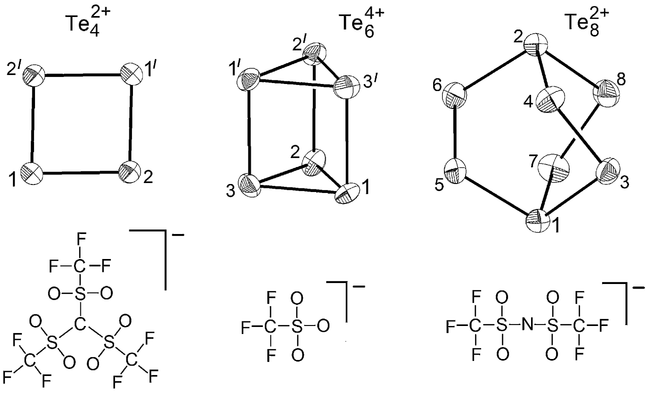

Figure 1. The structures of the three polycationic clusters obtained by electrochemical dissolution of elemental tellurium and the formulae of the respective anions tristriflylmethanide $[CTf_3]^-$, triflate $[OTf]^-$, and bistriflylimide $[NTf_2]^-$. Ellipsoids are set to 90% probability. [Te_4][$CTf_3]_2$: Symmetry operation for generating equivalent atoms: $I = 1-x$, $1-y$, $1-z$. Selected bond lengths [Å] and angles [°]: Te1–Te2 2.6671(3), Te2–Te1^I 2.6703(3); Te2-Te1-Te2^I 92.09(1), Te1-Te2-Te1^I 87.91(1). [Te_6][$OTf]_4$: Symmetry operation for generating equivalent atoms: $I = -x$, y, $-z$. Selected bond lengths [Å] and angles [°]: Te1–Te2 2.7235(4), Te2–Te3 2.6922(4), Te1–Te3 2.7203(4), Te1–Te3^I 3.0609(3), Te2–Te2^I 3.1346(5); Te1-Te2-Te3 60.30(1), Te2-Te3-Te1 60.42(1), Te3-Te1-Te2 59.28(1). [Te_8][$NTf_2]_2$: Only one of the two independent Te_8^{2+} cations is shown. Selected bond lengths [Å]: Te1–Te3 2.8327(7), Te1–Te5 2.7712(7), Te1–Te7 2.7969(7), Te2–Te4 2.7972(7), Te2–Te6 2.7835(7), Te2–Te8 2.8122(7), Te3–Te4 2.6586(7), Te5–Te6 2.6683(7), Te7–Te8 2.6666(8).

$[AsF_6]_4\cdot 2SO_2$, where the tellurium atoms are located in the higher coordinated bridging positions.[29] The unit cell of $[Te_8][NTf_2]_2$ contains two crystallographically independent $[Te_8]^{2+}$ ions with essentially identical structures (Supporting Information, Figure S8). $[Te_8][NTf_2]_2$ crystallizes in the acentric space group $P2_1$. Both of the two independent clusters are chiral and have the same axial enantiomorphy. The crystal itself is enantiomorphic, affirmed in the structure refinement by the Flack x parameter of $-0.03(1)$. During the crystallization process, a spontaneous separation of the enantiomorphs had occurred. Even though both independent clusters are located on general positions, the molecular symmetry D_3 is almost fulfilled. The average Te−Te bond length between a threefold-coordinated bridgehead tellurium atom and a twofold coordinated atom is 2.801 Å in the range 2.771 to 2.833 Å. As expected, the average bond length between the twofold coordinated atoms is shorter, namely 2.666 Å in the range 2.659 Å to 2.677 Å. Thus, all bond lengths are in the region of Te−Te single bonds, as found for diphenylditelluride (Te−Te 2.712(2) Å).[30] The bond lengths and angles within the bis(trifluoromethanesulfonyl)imide anion do not show any notable differences when compared to the respective alkali metal salts.[31]

^{125}Te NMR spectroscopy was applied to analyze the red–violet IL solutions before crystallization. This method has turned out to be appropriate and was already applied for tellurium polycation containing solutions.[32] Measured against $Te(CH_3)_2$ as external standard, only one single broad resonance at approximately +2700 ppm could be detected in the triflate approach as well as in the triflimide experiment. Schrobilgen et al. observed a signal at +2710 ppm for the $[Te_4]^{2+}$ cluster with a sharp signal enabling to determine Te-Te coupling constants.[32] This signal shift matches perfectly with the resonance observed in the experiment in the IL. Owing to the broad signal with full width at half maximum of more than 1000 Hz, couplings entirely disappear within the resonance. One reason for the large line width might be a valence fluctuation within the barrelane-shaped $[Te_8]^{2+}$ cluster.

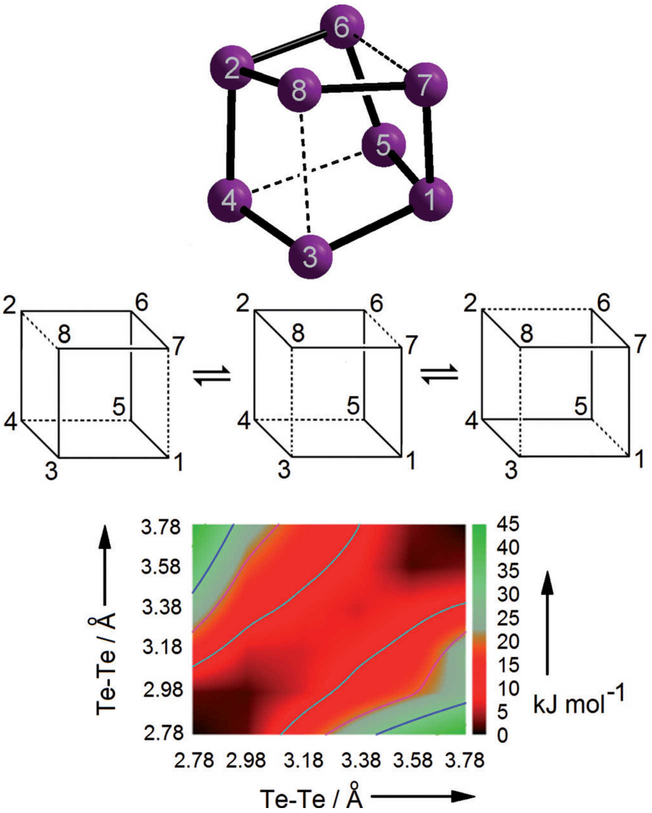

Figure 2. The structure of the $[Te_8]^{2+}$ cluster in $[Te_8][NTf_2]_2$ may be described as a distorted cube. The thick lines represent the regular Te−Te bonds between 2.6 and 2.8 Å, the dotted edges represent non-bonding Te⋯Te distances of 3.6 to 3.7 Å. By a concerted displacement of adjacent non-bonded Te atoms a dynamic valence fluctuation occurs, in which course all atoms take the role of the three-coordinated atoms and all atoms become equivalent. The two-dimensional potential energy surface for the valence isomerization was obtained on the B3LYP/TZVP level. The two coordinate axes refer to the Te1−Te7 and Te2−Te8 distances. The combination (3.78, 3.78) corresponds to the first structure, and (2.78, 2.78) corresponds to the second structure. The minimum energy path involves the simultaneous change of both distances. The center represents the transition-state structure (C_{2v} symmetry; Supporting Information, Figure S10) with all Te1–Te7, Te2–Te8, Te6–Te7, and Te3–Te8 distances equal to 3.28 Å.

To complement the spectroscopic results, the valence isomerization of $[Te_8]^{2+}$ was studied theoretically at density-functional theory level. Starting from the first structure as shown in the middle of Figure 2, a two-dimensional relaxed potential energy surface scan was performed using the distances Te1−Te7 and Te2−Te8 as parameters. The bond lengths were varied between 3.78 Å and 2.78 Å, which are the calculated distances of the first and the second structure, respectively (Supporting Information, Table S8). The corresponding potential energy surface is shown in Figure 2. Along the minimum energy path, the two bond lengths decrease simultaneously, accompanied by an increase of the Te3−Te8 and Te6−Te7 bond lengths. In the transition structure, the four bond lengths are equal (point group C_{2v}; Supporting Information, Figure S11). The calculated activation energy, 6–9 kJ mol^{-1} (Supporting Information, Table S10), is so small that transitions between the conformations are expected to be much faster than the time resolution of the NMR spectrometer, in agreement with the observed single resonance (Supporting Information, Figure S10). Other transition mechanisms between conformations with opposite chirality have been also studied. They involve a concerted rotation of two or three Te−Te bonds and lead to transition states with C_s and D_{3h} symmetry, respectively (Supporting Information, Figure S12). However, the activation barriers connected with these rearrangements, 96 and 144 kJ mol^{-1}, respectively, are much larger than for the valence isomerization so that they will not play a significant role. At the same time the calculated isotropic chemical shifts of all Te atoms of the $[Te_8]^{2+}$ cluster are within a few ppm despite their different environments (Supporting Information, Table S9). This slight variation gives a possible explanation for the relatively large band width (see below).

In summary, we have demonstrated that the anodic oxidation of elemental tellurium in ionic liquids consisting of alkyl ammonium or alkyl imidazolium cations and the trifluoromethanesulfonyl anions $[OTf]^-$, $[NTf_2]^-$, and $[CTf_3]^-$ gives access to the polycationic clusters $[Te_4]^{2+}$ (square planar), $[Te_6]^{4+}$ (prismatic), and the novel $[Te_8]^{2+}$ bearing a barrelane-shaped structure. The electrochemical method of oxidation allows for the synthesis of salt-like compounds made up of chalcogen polycations and common weakly coordinating anions, which were not available by the so far generally used route to these clusters, that is, the oxidation of elemental chalcogen with a respective higher halide in presence of a strong Lewis acid. The examination of $[Te_8]^{2+}$ by ^{125}Te NMR spectroscopy in solution revealed a highly dynamic molecule with fast valence isomerization. DFT calculations disclose a mechanism with a very low energy barrier between the isomeric forms.

Experimental Section

Detailed descriptions of the syntheses of the ionic liquids and the equipment and procedures of the electrochemical dissolution of elemental tellurium are collected in the Supporting Information.

The crystal structures were solved by direct methods and refined based on F^2 with anisotropic displacement parameters for all atoms.[33] A semi-empirical absorption correction was applied to the data set.[34] Data collections were performed at $-150\,°C$ (123 K).

Crystal structure determination of $[Te_4][CTf_3]_2$: $C_8F_{12}O_{12}S_6Te_4$, $Z=2$, monoclinic, $P2_1/n$, $a=7.9803(1)$, $b=12.3918(2)$, $c=15.7544(3)$ Å, $\beta=99.971(1)°$, 3513 independent reflections in the range $2.91° < \theta < 27.49°$, 218 parameters, $R(|F|)$ for $F_o > 4\sigma(F_o)$ 0.0262, $R(|F|)$ for all reflections 0.0367, $wR(F^2)$ 0.0524, max. and min. residual density $0.72/-0.72$ e Å^{-3}.

Crystal structure determination of $[Te_6][OTf]_4$: $C_4F_{12}O_{12}S_4Te_6$, $Z=2$, monoclinic, $C2$, $a=14.0500(1)$, $b=8.4764(1)$, $c=11.0485(1)$ Å, $\beta=108.314(1)°$, 2875 independent reflections in the range $2.91° < \theta < 27.49°$, 173 parameters, $R(|F|)$ for $F_o > 4\sigma(F_o)$ 0.0155, $R(|F|)$ for all reflections 0.0158, $wR(F^2)$ 0.0362, max. and min. residual density $0.63/-0.54$ e Å^{-3}, Flack x parameter 0.46(2), indicating that the examined crystal was a racemic twin.

Crystal structure determination of $[Te_8][NTf_2]_2$: $C_4F_{12}N_2O_8S_4Te_8$, $Z=4$, monoclinic, $P2_1$, $a=10.5458(1)$, $b=11.9702(1)$, $c=22.7573(1)$ Å, $\beta=96.477(1)°$, 16671 independent reflections in the range $2.91° < \theta < 30.03°$, 686 parameters, $R(|F|)$ for $F_o > 4\sigma(F_o)$ 0.0280, $R(|F|)$ for all reflections 0.0343, $wR(F^2)$ 0.0592, max. and min. residual density $1.38/-1.12$ e Å^{-3}, Flack x parameter 0.028(13).

Further details of the crystal structure determinations are included in the Supporting Information and have been deposited with the Fachinformationszentrum FIZ Karlsruhe (76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de). These data may be obtained by quoting the depository numbers CSD-429954 for $(Te_4)(CTf_3)_2$, CSD-429955 for $(Te_6)(OTf)_4$, and CSD-429956 for $(Te_8)(NTf_2)_2$.

The quantum-chemical calculations were performed with the B3LYP functional and a triple-zeta basis set employing the Gaussian09 program suite. For further details on the quantum chemical calculations, see the Supporting Information.

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