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Tellurium Dications

Tellurium(II)-Centered Dications from the Pseudohalide "Te(OTf)$_2$"**

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Dedicated to Professor Ronald Gillespie on the occasion of his 85th birthday

The synthesis and isolation of p-block polycations is a new frontier of chemistry that is driven by the potential for discovering unprecedented structure, bonding, and reactivity for the main-group elements. There have been several notable successes in this area over the past two years, with reports of tricationic B^{III}, dicationic B^{III}, Al^{III}, Ge^{II}, P^{V}, S^{II}, and Se^{II} centered complexes (e.g. **1**–**6**; Figure 1).[1–6] The general strategy for realizing such species involves the reaction of a strong Lewis base with a Lewis acidic p-block element precursor, resulting in the delocalization of the polycationic charge and making the salts isolable.

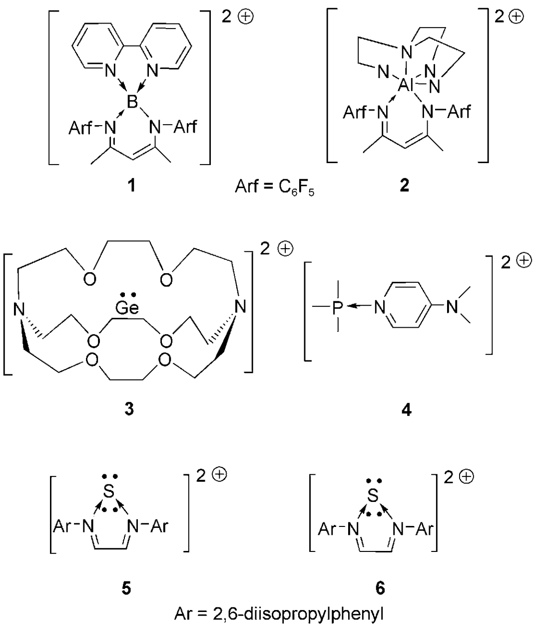

Figure 1. Examples of main-group-element centered dications.

For the heavier Group 16 elements (Se, Te) this approach is more complex as the obvious source for a dicationic chalcogen is the tetrahalides (EX_4; E = Se, Te; X = Cl, Br, I) which would be the Lewis acidic starting materials. Unfortunately, these compounds readily undergo redox reactions in the presence of strong Lewis bases, often to the elemental form, precluding access to the target compounds.[7–10] Nevertheless, success in generating highly charged (dicationic) S and Se species has been achieved by utilizing low-valent dihalides as the chalcogen source (SCl_2 or $SeCl_2$).[11] For tellurium, no stable binary dihalide reagents are known, thus developing the corresponding chemistry for this heavier congener has remained elusive. Cowley and Reeske recently reported the isolation of what can be described as a trapped TeI_2 species (**7**; Figure 2), which was of great interest to our group as it appeared to have the potential to act as an ideal source of Te^{II}.[12] Despite intensive efforts, we have had no success in cleanly liberating the TeI_2 from the N,N′ chelate, which is a testament to the instability of TeX_2. In this context, we now report our work in utilizing Cowley's "TeI_2" for the synthesis and isolation of a unique base-stabilized "Te(OTf)$_2$" (**8**; Figure 2), which could have immense synthetic utility as

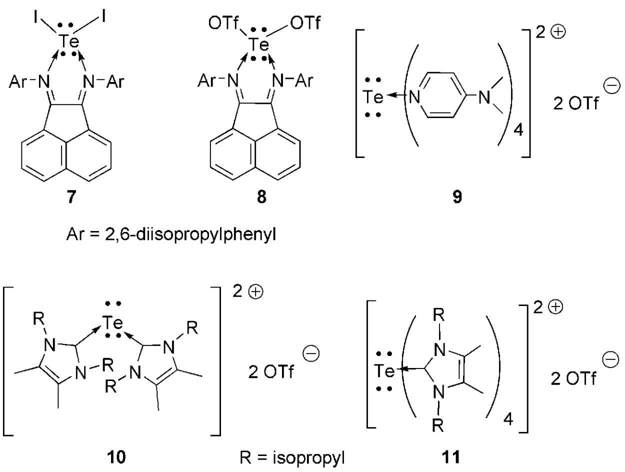

Figure 2. Base-stabilized "TeI_2" and "Te(OTf)$_2$" species **7** and **8** and tellurium-centered dications **9**–**11**.

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the first tellurium dihalide-like synthon. As a demonstration of the potential for such a reagent, we have exploited this compound in the synthesis of unprecedented molecular architectures for the Group 16 elements (**9**–**11**; Figure 2). Compounds **9** and **11** are rare examples of a main-group element pinwheel coordination complexes, and **10** is an isovalent dicationic, Group 16 analogue of the recently reported carbodicarbene.[13] These compounds represent the first tellurium(II)-centered dications and demonstrates the efficacy of the [LTe(OTf)$_2$] (L = bidentate ligand) synthon in the discovery of new structure and bonding for the p-block elements.

The reaction of **7** ([Dipp$_2$BIANTeI$_2$]; Dipp = 2,6-diisopropylphenyl; BIAN = bis(arylimino)acenaphthene) with an excess (2.5 equiv) of AgOTf in CH_2Cl_2 resulted in a rapid (5 min) and distinct color change from blue, through purple, and ultimately to a deep red. Separation of the supernatant solution from the silver-salt byproducts followed by addition of *n*-pentane to the solution, resulted in the precipitation of a dark red powder. A sample of the dried solid was redissolved in $CDCl_3$ for ^{1}H NMR spectroscopy, which revealed a set of resonances consistent with a single compound containing the Dipp$_2$BIAN ligand. The signals arising from the BIAN backbone were shifted slightly downfield with respect to the TeI_2 complex (avg. $\Delta\delta = 0.1$ ppm). In both the ^{19}F{^{1}H} and ^{125}Te{^{1}H} NMR spectra only one signal was observed at $\delta = -78.3$ ppm and $\delta = 2853$ ppm, respectively. This extremely downfield resonance in the ^{125}Te{^{1}H} NMR spectrum pointed to an electron poor Te center. Conclusive identification of the compound as the Dipp$_2$BIAN-trapped TeOTf$_2$ complex **8** was ascertained through X-ray diffraction studies (Figure 3) of single crystals grown by the vapor diffusion of Et_2O into concentrated CH_2Cl_2 solutions of the bulk powder.

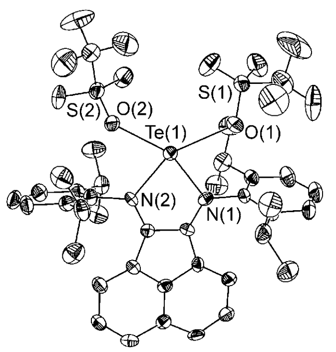

Figure 3. Solid-state structure of **8**. Thermal ellipsoids are set at 50% probability, hydrogen atoms and CH_2Cl_2 solvate are omitted for clarity. Selected bond lengths [Å] and angles [°] [calculated values in square brackets]: Te(1)–N(1) 2.151(4) [2.039], Te(1)–N(2) 2.182(4) [2.039], Te(1)–O(1) 2.329(4), Te(1)–O(2) 2.471(4); O(1)-Te(1)-(O2) 126.3(1), N(1)-Te(1)-N(2) 75.9(2) [80.1].[14]

To examine the synthetic utility of the Te(OTf)$_2$ species we sought to displace the triflate anions from tellurium. The reaction of **8** with four equivalents of 4-DMAP (DMAP = 4-dimethylaminopyridine) resulted in an immediate color change from red to yellow. The subsequent addition of Et_2O yielded a colorless powder, which was collected and dried in vacuo. A sample of the powder was dissolved in $CDCl_3$ for ^{1}H NMR spectroscopy, and revealed signals consistent with a product containing 4-DMAP moieties and no evidence of Dipp$_2$BIAN. The signals were shifted downfield from free 4-DMAP ($\Delta\delta = 0.46$, 0.07, 0.09 ppm) and only one triflate signal was observed in the ^{19}F{^{1}H} NMR spectrum, at a chemical shift indicative of distinct cation–anion separation in solution ($\delta = -78.9$ ppm, c.f. [Bu$_4$N][OTf] $\delta = -79.0$ ppm (ionic) and (CH$_3$)$_3$Si-OTf $\delta = -77.7$ ppm (covalent)). In the ^{125}Te{^{1}H} NMR spectrum the single resonance was found to be shifted slightly upfield from compound **8** ($\delta = 2750$ ppm). Single crystals were grown from a concentrated CH_2Cl_2 solution of the powder by vapor diffusion of Et_2O. Subsequent X-ray diffraction studies confirmed the production of a Te^{II} centered dication (**9**; Figure 4), which could be isolated in 75% yield.

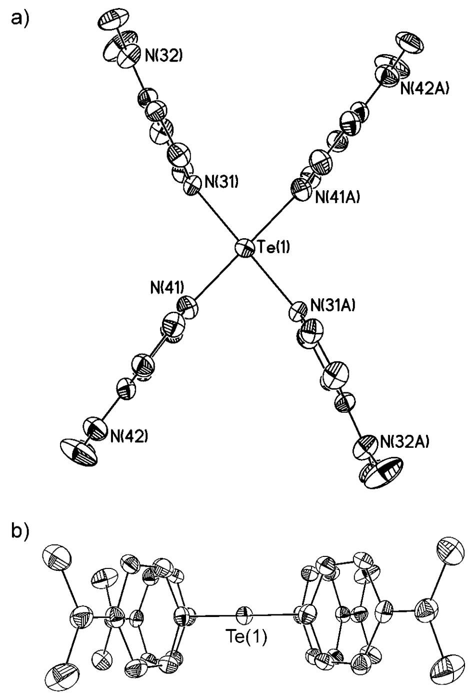

Figure 4. a,b) Two views of the solid-state structure of **9**, showing one of two independent cations in the asymmetric unit. Thermal ellipsoids are set at 30% probability. Triflate anions, hydrogen atoms and CH_2Cl_2 solvate are omitted for clarity. Selected bond lengths [Å] and angles [°] [calculated values in square brackets]: Te(1)–N(31) 2.308(5) [2.317], Te(1)–N(41) 2.313(6) [2.317], N(41)-Te(1)-N(31) 97.0(2), N(31)-Te(1)-N(41A) 83.0(2).[14]

The reaction of **8** with two equivalents of the N-heterocyclic carbene 2,5-diisopropylimidazole-3,4-dimethyl-2-ylidene (*i*PrIM) resulted in an immediate color change from red to yellow, the addition of Et_2O and *n*-pentane gave a pale yellow precipitate. Proton NMR spectroscopy of a redissolved sample of the precipitate showed resonances arising from the NHC ligand but again no evidence of Dipp$_2$BIAN. As in the case of **9**, the resonances of the carbene were shifted significantly downfield from the free ligand ($\Delta\delta(i\mathrm{Pr}_{C\text{-}H}) =$

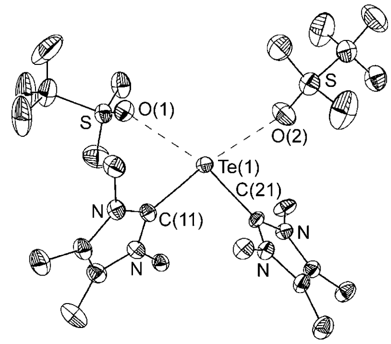

Figure 5. Solid-state structure of **10**. Thermal ellipsoids are set at 50% probability, methyl substituents on the *i*Pr groups and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] [calculated values in square brackets]: Te(1)–C(11) 2.136(4) [2.109], Te(1)–C(21) 2.138(3) [2.109], Te(1)···O(1) 2.921(3), Te(1)···O(2) 2.740(3); C(11)-Te(1)-C(21) 91.5(1) [99.8]. Angle [°] between planes defined by C(11)-Te(1)-C(21) and O(1)-Te(1)-O(2) 10.6.[14]

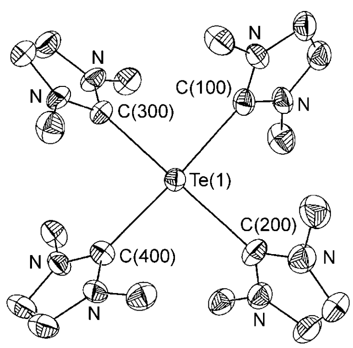

Figure 6. Solid-state structure of compound **11**. Thermal ellipsoids are set at 50% probability, triflate anions, THF solvate, hydrogen atoms and methyl substituents are removed for clarity. Selected bond lengths [Å] and angles [°]: Te(1)–C(100) 2.470(6), Te(1)–C(200) 2.519(7), Te(1)–C(300) 2.342(6), Te(1)–C(400) 2.415(6); C(100)-Te(1)-C(200) 91.3(2), C(200)-Te(1)-C(400) 91.5(2), C(400)-Te(1)-C(300) 88.2(2), C(300)-Te(1)-C(100) 88.9(2).[14]

1.27 ppm). X-ray diffraction studies on single crystals grown from the bulk powder revealed a tellurium-centered dication, featuring two NHC ligands bound to the Te atom (**10**; Figure 5). If two additional equivalents of the NHC are allowed to react with **10**, a square planar Te dication bearing four carbene substituents is formed (**11**; Figure 6), analogous to compound **9**.

The solid-state structure of complex **8** reveals a square-planar TeN_2O_2 core. This arrangement is imposed by the AX_4E_2 electron-pair formula, common to 12-electron chalcogen centers. The Te–N bond lengths are significantly shorter than those found in the TeI_2 congener (2.151(4), 2.182(4) Å; c.f. 2.40 Å in **7**), reflecting the stronger σ-donor ability of I^- compared to OTf^-. The Te–O distances are very long (2.329(4), 2.471(4) Å), compared with a standard Te–O bond length of 1.95 Å.[15] However, based on the clear difference in the ^{19}F NMR spectrum of purely ionic triflate, we concluded that the triflate substituents remain weakly associated with the tellurium in solution. The solid-state structure of **9** features a central Te^{II} dication surrounded by four 4-DMAP ligands in an essentially perfect square-planar bonding arrangement (Σ(angles) = 360°). The structure has four, nearly equivalent Te–N bonds of 2.27–2.31 Å, with all of the 4-DMAP ligands orientated perpendicular to the pseudo C_4 principal axis of rotation. There are distant Te···O contacts of greater than 4 Å, well outside the sum of the van der Waals radii (3.60 Å). This "pinwheel" bonding motif defined by the pyridine ligands has been observed in a number of transition-metal species, but compound **9** is only the third p-block system isolated in such a bonding arrangement, and the sole example from Group 16.[16–18]

The solid-state structure of compound **10** displays a tellurium-centered dication bound by two NHC ligands. The compound can be considered an isovalent heavy-atom analogue of the "bent allene" (**12a**) or "carbodicarbene" (**12b**) recently reported by Bertrand et al.[13] The differences in the electronic structures between **12** and the Te species are clearly shown by the geometric parameters, where the C(11)-Te(1)-C(21) angle is 91.5(1)°, as compared to 134° for the carbon(0) example. In valence bond terms, this reflects the use of completely unhybridized orthogonal p orbitals to form the Te–C bonds in **10**. The Te–C distances in **10** (2.136(4), 2.138(3) Å) are consistent with single bonds as they display no shortening indicative of multiple bond character and are similar to other representative Te–C single bonds (ca. 2.10 Å).[10,19] This underscores the difference in structure from **12**, in that **10** cannot be represented as an analogue of **12a**, but is best drawn as a heavy-element analogue of **12b** (Figure 7).[13,20,21] There are only weak solid-state interactions with the oxygen atoms of the OTf anions of at least 2.74 Å, and the O atoms involved (O(1), O(2)) are distorted significantly outside the ideal square plane about the tellurium center.

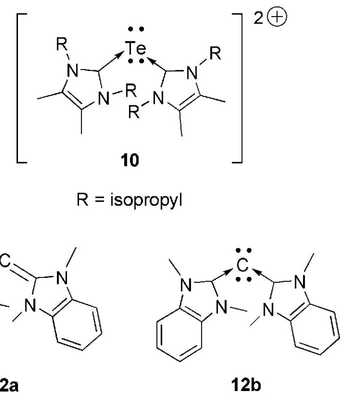

Figure 7. The two extremes in the bonding description of the carbodicarbene **12**, compared with the description of Te dication **10**.

The Te–C bond lengths in **11** were found to be significantly longer than those in **10**, ranging from 2.342(6) Å to 2.519(7) Å. The elongation of the bonds is driven by the much stronger *trans* influence of the additional carbene ligands, as compared to the weak interactions with the triflate anions in the solid state for **10**. The overall geometry about the Te center is square planar (Σ(angles) = 359.9°), analogous to compound **9**.

The electronic structure and bonding in the dications of **8**–**10** was also assessed with theoretical methods. Calculations were performed at the density functional theory (DFT) level and using PBE1PBE exchange-correlation functional together with def2-TZVPP basis sets. For reasons of computational efficiency, isopropyl and diisopropylphenyl groups were replaced with methyl and phenyl, respectively. The optimized geometrical parameters are in good agreement with the experimental data for compounds **9** and **10** taking into account the neglect of counterions and that simplified model systems were used. Less agreement between the observed and calculated parameters was found for **8**, reflecting the covalent bonding interaction between the triflate ions and Te. Natural population analysis shows that the calculated atomic charge at the tellurium atom varies from +0.65 ($\mathbf{10}^{2+}$) to +1.22 ($\mathbf{8}^{2+}$) in line with the experimentally observed strength of cation–anion interactions in these systems.

The electronic structure of the dications is perhaps best illustrated by visualizing their electron localization functions (ELFs) which show two monosynaptic, lone pair, valence basins at the tellurium, V(Te). The ELF of $\mathbf{10}^{2+}$ is shown in Figure 8; the ELFs of $\mathbf{8}^{2+}$ and $\mathbf{9}^{2+}$ are included as Supporting Information. The population of the V(Te) basins is 2.3 electrons each, which conforms well to the description of two localized electron pairs, one above and one below the plane formed by the tellurium center and atoms directly bonded to it.

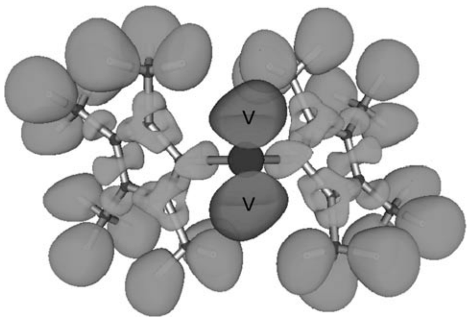

Figure 8. The electron localization function of $\mathbf{10}^{2+}$ (isosurface value 0.80). Monosynaptic V(Te) valence basins are labeled V.

Herein we have described a unique example of a molecular p-block triflate (**8**), which can be sequestered and shuttled between different Lewis bases, and thus can be considered a synthetic source of $TeOTf_2$. This stable, electrophilic form of Te^{II} can be utilized in the synthesis of highly novel main-group compounds such as the Te^{II} centered dications **9**–**11**. These reactions show no propensity for the reduction of Te to the elemental state, thus opening the door to new synthetic opportunities in organic and inorganic tellurium chemistry.

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[14] Crystal data for **8**: Formula = $C_{39}H_{42}Cl_2F_6N_2O_6S_2Te$, T = 150(2) K, M_r = 1011.37 g mol^{-1}, crystal size: 0.31 × 0.26 × 0.08 mm, orthorhombic, space group *Pna*2(1), a = 18.491(4), b = 12.156(2), c = 19.453(4) Å, V = 4372(2) Å^3, Z = 4, ρ_{calcd} = 1.536 g cm^{-3}, μ = 0.969 mm^{-1}, $2\theta_{max}$ = 27.49°, 9395 reflections measured, 9395 unique, refined parameters = 524, $R_1[(I) > 2\sigma(I)]$ = 0.0524, w$R_2(F^2)$ = 0.1146, R_1(all data) = 0.0875, wR_2(all data) = 0.1310, ρ(e)(min/max) = −1.183/0.970 e Å^{-3}. Crystal data for **9**: Formula = $C_{31.5}H_{42}F_6N_8O_6S_2Te$, T = 150(2) K, M_r = 1040.80 g mol^{-1}, crystal size: 0.30 × 0.30 × 0.20 mm, triclinic, space group $P\bar{1}$, a = 12.134(2), b = 13.834(3), c = 14.387(3) Å, α = 66.67(3), β = 86.23(3), γ = 78.03(3)°, V = 2169.1(8) Å^3, Z = 2, ρ_{calcd} = 1.594 g cm^{-3}, μ = 1.043 mm^{-1}, $2\theta_{max}$ = 25.16°, 11185 reflections measured, 7721 unique (R_{int} = 0.0549), refined parameters = 531, $R_1[(I) > 2\sigma(I)]$ = 0.0682, w$R_2(F^2)$ = 0.1727, R_1-(all data) = 0.1327, wR_2(all data) = 0.2006, ρ(e)(min/max) = −1.022/1.180 e Å^{-3}. Crystal data for **10**: Formula = $C_{24}H_{40}F_6N_4O_6S_2Te$, T = 150(2) K, M_r = 786.32 g mol^{-1}, crystal size: 0.41 × 0.35 × 0.29 mm, monoclinic, space group *P*21/*c*, a = 12.353(3), b = 18.018(4), c = 14.965(3) Å, β = 97.08(3)°, V = 3305(1) Å^3, Z = 4, ρ_{calcd} = 1.580, μ = 1.102 mm^{-1}, $2\theta_{max}$ =

27.62°,12785 reflections measured, 7565 unique ($R_{int}=0.0345$), refined parameters = 400, $R_1[(I)>2\sigma(I)]=0.0453$, $wR_2(F^2)=0.1032$, R_1(all data) = 0.0673, wR_2(all data) = 0.1139, ρ(e)(min/max) = −0.940/1.122 e Å^{-3}. Crystal data for **11**: Formula = $C_{54}H_{96}F_6N_8O_8S_2Te$, $T=150(2)$ K, $M_r=1291.11$ g mol^{-1}, crystal size: 0.25 × 0.20 × 0.18 mm, monoclinic, space group $P21/c$, $a=18.240(3)$, $b=16.329(3)$, $c=24.558(9)$ Å, $\beta=118.87(2)°$, $V=6405(3)$ Å^3, $Z=4$, $\rho_{calcd}=1.339$, $\mu=0.601$ mm^{-1}, $2\theta_{max}=25.02°$, 21898 reflections measured, 11278 unique ($R_{int}=0.0748$), refined parameters = 712, $R_1[(I)>2\sigma(I)]=0.0688$, $wR_2(F^2)=0.1801$, R_1(all data) = 0.1303, wR_2(all data) = 0.2201, ρ(e)(min/max) = −0.951/1.349 e Å^{-3}. CCDC 711250 (**8**), 711251 (**9**), 719664 (**10**), 722582 (**11**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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