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Tellurium(II) centered dications from the novel pseudohalide TeOTf₂**

Jason L. Dutton, Heikki M. Tuononen and Paul J. Ragnogna*

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**).^[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 rendering the salts isolable.

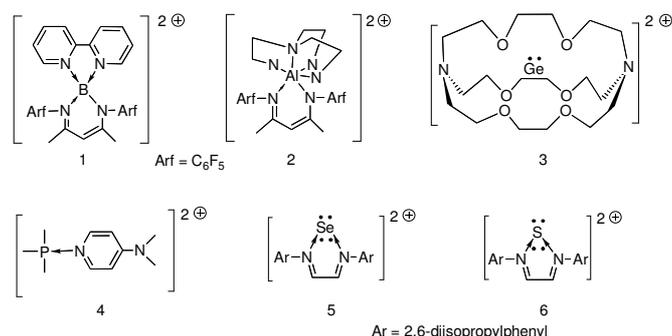
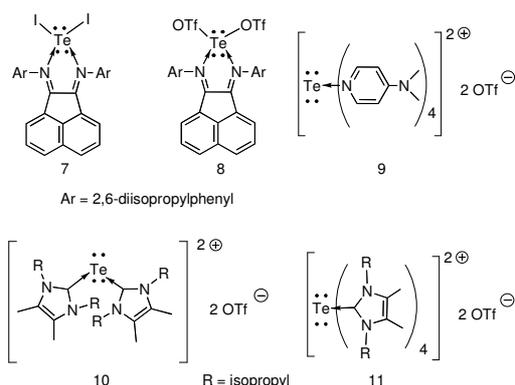


Figure 1. Examples of main group centered dications.

For the heavier group 16 elements (Se, Te) this approach is more complex as the obvious source for a dicationic chalcogen resides with the tetrahalides as the Lewis acidic starting materials (ChX₄; Ch = Se, Te; X = Cl, Br, I). 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 (SCl₂ or SeCl₂).^[11] For tellurium, no stable binary dihalide reagents are known, thus developing the corresponding chemistry for this heavier congener has remained elusive. Cowley et al. recently reported the isolation of what can be described as a trapped TeI₂ species (**7**), 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 TeI₂ from the *N,N'* chelate, which is a testament to the instability of TeX₂. In this context, we now report our work in utilizing Cowley's "TeI₂" for the synthesis and isolation of a unique base stabilized TeOTf₂ (**8**), which could have immense synthetic utility as the first tellurium dihalide-like synthon. As a demonstration of the potential for such a reagent, we have exploited this unique compound in the synthesis of unprecedented molecular architectures for the group 16 elements (**9-11**). Compound **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] All of these compounds represent the first Te(II) centered dications and demonstrates the efficacy of the L₂TeOTf₂ synthon in the discovery of new structure and bonding for the p-block elements.

The reaction of **7** (Dipp₂BIAN-TeI₂; Dipp = 2,6-diisopropylphenyl; BIAN = bis(arylimino)acenaphthene) with an excess (2.5 equiv.) of AgOTf in CH₂Cl₂ resulted in a rapid (5 min.) and distinct color change from blue, through purple and ultimately to a deep red. Separation of the supernatant from the silver salt byproducts followed by addition of *n*-pentane, resulted in the precipitation of a



dark red powder. A sample of the dried solid was redissolved in CDCl₃ for ¹H NMR spectroscopy, which revealed a set of resonances consistent with a single compound containing the Dipp₂BIAN ligand. The signals arising from the BIAN backbone were shifted slightly downfield with respect to the TeI₂ complex (avg. Δδ = 0.1 ppm). In both the ¹⁹F{¹H} and ¹²⁵Te{¹H} NMR spectra only one signal was observed at δ = -78.3 ppm and δ = 2853 ppm, respectively. This extremely low-field resonance in the ¹²⁵Te{¹H} NMR pointed to an electron poor Te center. Conclusive identification of the compound as the Dipp₂BIAN trapped TeOTf₂ complex (**8**; Figure 2) was ascertained through X-ray diffraction studies of single crystals grown by the vapor diffusion of Et₂O into concentrated CH₂Cl₂ solutions of the bulk powder.

In an effort to examine the synthetic utility of the TeOTf₂, we sought to displace the triflate anions from tellurium. The reaction of compound **8** with four stoichiometric equivalents of 4-DMAP (DMAP = 4-dimethylaminopyridine) resulted in an immediate color change from red to yellow. The subsequent addition of Et₂O yielded a colorless powder, which was collected and dried in vacuo. A sample of the powder was dissolved in CDCl₃ for ¹H NMR spectroscopy, and revealed signals consistent with a product containing only 4-DMAP and no evidence of Dipp₂BIAN. The

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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 $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum, indicative of distinct cation-anion separation in solution ($\delta = -78.9$ ppm, *c.f.* $[\text{Bu}_4\text{N}][\text{OTf}] = -79.0$ ppm (ionic) and $(\text{CH}_3)_3\text{Si-OTf} = -77.7$ ppm (covalent)). The $^{125}\text{Te}\{^1\text{H}\}$ 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 via vapor diffusion of Et_2O . Subsequent X-ray diffraction studies confirmed the production of a Te(II) centered dication (**9**; Figure 3), isolated in 75% yield.

The reaction of **8** with two equivalents of the N-heterocyclic carbene 2,5-diisopropylimidazole-3,4-dimethyl-2-ylidene ($^i\text{PrIM}$) 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 again showed no evidence of Dipp_2BIAN , only resonances arising from the NHC ligand were present. As in the case of **9**, the resonances of the carbene were shifted significantly downfield from the free ligand ($\Delta\delta(i\text{PrC-H}) = 1.27$ ppm). X-ray diffraction studies on single crystals grown from the bulk powder revealed a Te centered dication, featuring two NHC ligands bound to the Te atom (**10**; Figure 4). If two additional stoichiometric equivalents of the NHC are reacted with **10**, a square planar Te dication bearing four carbene substituents is formed (**11**; Figure 6), analogous to compound **9**.

Compounds **8-11** have been studied by single crystal X-ray diffraction studies.^[14] 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) Å; 2.182(4) Å; *c.f.* 2.40 Å in **7**), reflecting the stronger σ donor ability of I⁻ as compared to OTf^- . The Te-O distances are very long (2.329(4) Å; 2.471(4) Å), compared with a standard Te-O bond distance 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

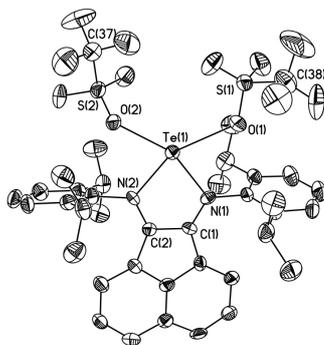


Figure 2. Solid-state structure of **8**. Ellipsoids are drawn to 50% probability, hydrogen atoms and CH_2Cl_2 solvate are omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$) [calculated values in square brackets]: Te(1)-N(1) 2.151(4) [2.039], Te(1)-N(2) 2.182(4) [2.039], Te(1)-O(1) 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].

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 ($\Sigma(\text{angles}) = 360^\circ$). The structure has four, nearly equivalent Te-N bond lengths 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 $\text{Te}\cdots\text{O}$ 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]

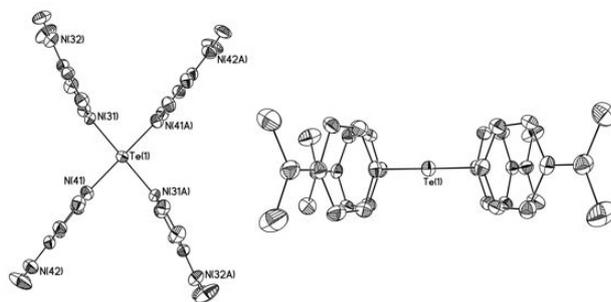


Figure 3. Two views of the solid-state structure of **9**, showing one of two independent cations in the asymmetric unit. Ellipsoids are drawn to 30% probability. Triflate anions, hydrogen atoms and CH_2Cl_2 solvate are omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$) [calculated 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) [90.0], N(31)-Te(1)-N(41A) 83.0(2) [90.0].

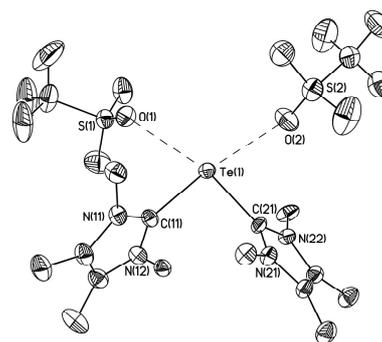


Figure 4. Solid-state structure of **10**. Ellipsoids are drawn to 50% probability, methyl substituents on the ‘Pr groups and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles ($^\circ$) [calculated values in square brackets]: Te(1)-C(11) 2.136(4) [2.109], Te(1)-C(21) 2.138(3) [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 ($^\circ$) between planes defined by C(11)-Te(1)-C(21) and O(1)-Te(1)-O(2) 10.6.

The solid state structure of compound **10** displays a Te centered dication bound by two NHC ligands. The compound can be considered an isovalent heavy atom analogue of the recently reported “bent allene” (**12a**) or “carbodicarbene” (**12b**) reported by Bertrand et al.^[13] The differences in the electronic structures between **12** and the Te species are clearly shown by the metrical parameters, where the C(11)-Te(1)-C(21) angle is $91.5(1)^\circ$, 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 (≈ 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 5).^[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.

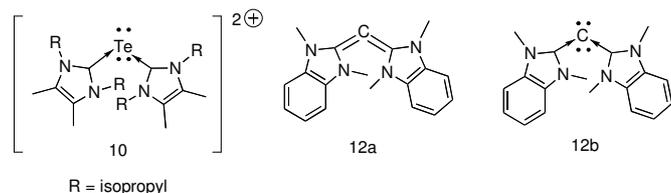


Figure 5. The two extremes in the bonding description of the carbodicarbene **12**, compared with the description of Te dication **10**.

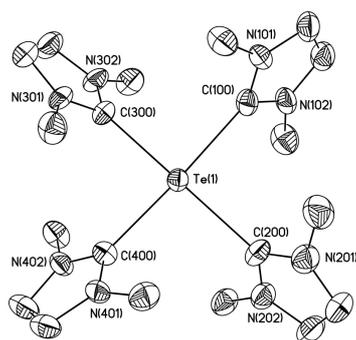


Figure 6. Solid state structure of compound **11**. Ellipsoids are drawn to 50% probability, triflate anions, THF solvate, hydrogen atoms and methyl substituents are removed for clarity. Selected bond lengths [Å] and angles [°]: Te(1)-C(100) 2.470(6), Te(1)-C(200) 2.519(7), Te(1)-C(300) 2.342(6), Te(1)-C(400) 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).

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 ($\Sigma(\text{angles}) = 359.9^\circ$), 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 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 metrical parameters was found for **8**, reflecting the covalent bonding interaction between the triflates and Te. Natural population analysis shows that the calculated atomic charge at the tellurium atom varies from +0.65 (10^{2+}) to +1.22 (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, $V(\text{Te})$. The ELF of 10^{2+} is shown in Figure 7; the ELFs of 8^{2+} and 9^{2+} are included as Supporting Information. The population of the $V(\text{Te})$

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.

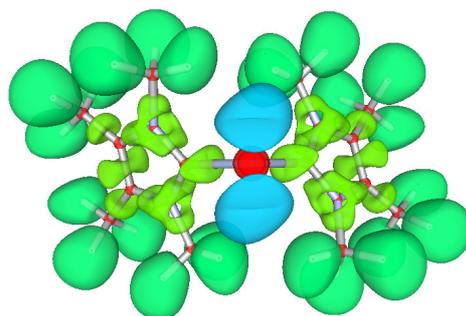


Figure 7. The electron localization function of 10^{2+} (isosurface value 0.80). Monosynaptic $V(\text{Te})$ valence basins are shown in blue.

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 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) centred 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 = $C_{39}H_{42}Cl_2F_6N_2O_6S_2Te_1$, $T = 150(2)$ K, $M_r = 1011.37$ g mol⁻¹, crystal size: $0.31 \times 0.26 \times 0.08$ mm, orthorhombic, space group $Pna2(1)$, $a = 18.491(4)$, $b = 12.156(2)$, $c = 19.453(4)$ Å, $V = 4372(2)$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 1.536$ g cm⁻³, $\mu = 0.969$ mm⁻¹, $2\theta_{\text{max}} = 27.49^\circ$, 9395 reflections measured, 9395 unique, refined parameters = 524, $R_I[(I) > 2\sigma(I)] = 0.0524$, $wR_2(F^2) = 0.1146$, $R_I(\text{all data}) = 0.0875$, $wR_2(\text{all data}) = 0.1310$, $\rho(e)(\text{min/max}) = -1.183/0.970$ e Å⁻³. Crystal data for **9**: Formula = $C_{31.5}H_{42}F_6N_8O_6S_2Te_1$, $T = 150(2)$ K, $M_r = 1040.80$ g mol⁻¹, crystal size: $0.30 \times 0.30 \times 0.20$ mm, triclinic, space group $P-1$, $a = 12.134(2)$, $b = 13.834(3)$, $c = 14.387(3)$ Å, $\alpha = 66.67(3)$, $\beta = 86.23(3)$, $\gamma = 78.03(3)^\circ$, $V = 2169.1(8)$ Å³, $Z = 2$, $\rho_{\text{calcd}} = 1.594$ g cm⁻³, $\mu = 1.043$ mm⁻¹, $2\theta_{\text{max}} = 25.16^\circ$, 11185 reflections measured, 7721 unique ($R_{\text{int}} = 0.0549$), refined parameters = 531, $R_I[(I) > 2\sigma(I)] = 0.0682$, $wR_2(F^2) = 0.1727$, $R_I(\text{all data}) = 0.1327$, $wR_2(\text{all data}) = 0.2006$, $\rho(e)(\text{min/max}) = -1.022/1.180$ e Å⁻³. Crystal data for **10**: Formula = $C_{24}H_{40}F_6N_4O_6S_2Te_1$, $T = 150(2)$ K, $M_r = 786.32$ g mol⁻¹, crystal size: $0.41 \times 0.35 \times 0.29$ mm, monoclinic, space group $P2(1)/c$, $a = 12.353(3)$, $b = 18.018(4)$, $c = 14.965(3)$ Å, $\beta = 97.08(3)$ Å, $Z = 4$, $\rho_{\text{calcd}} = 1.580$, $\mu = 1.102$ mm⁻¹, $2\theta_{\text{max}} = 27.62^\circ$, 12785 reflections measured, 7565 unique ($R_{\text{int}} = 0.0345$), refined parameters = 400, $R_I[(I) > 2\sigma(I)] = 0.0453$, $wR_2(F^2) = 0.1032$, $R_I(\text{all data}) = 0.0673$, $wR_2(\text{all data}) = 0.1139$, $\rho(e)(\text{min/max}) = -0.940/1.122$ e Å⁻³. Crystal data for **11**: Formula = $C_{54}H_{96}F_6N_8O_8S_2Te_1$, $T = 150(2)$ K, $M_r = 1291.11$ g mol⁻¹, crystal size: $0.25 \times 0.20 \times 0.18$ mm, monoclinic, space group $P2(1)/c$, $a = 18.240(3)$, $b = 16.329(3)$, $c = 24.558(9)$ Å, $\beta = 118.87(2)$ Å, $V = 6405(3)$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 1.339$, $\mu = 0.601$ mm⁻¹, $2\theta_{\text{max}} = 25.02^\circ$, 21898 reflections measured, 11278 unique ($R_{\text{int}} = 0.0748$), refined parameters = 712, $R_I[(I) > 2\sigma(I)] = 0.0688$, $wR_2(F^2) = 0.1801$, $R_I(\text{all data}) = 0.1303$, $wR_2(\text{all data}) = 0.2201$, $\rho(e)(\text{min/max}) = -0.951/1.349$ 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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