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ARTICLE TYPE

A planar dianionic ditelluride and a cyclic tritelluride supported by P_2N_2 rings†

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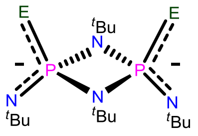
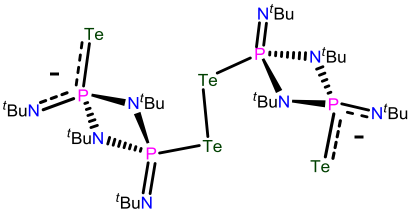
Oxidation of alkali metal derivatives of $[\mathrm{Te}(^t\mathrm{BuN})\mathrm{P}(\mu\text{-N}^t\mathrm{Bu})_2\mathrm{P}(\mathrm{N}^t\mathrm{Bu})\mathrm{Te}]^{2-}$ with I_2 produces the intermediate ditelluride dianion $[\mathrm{Te}(^t\mathrm{BuN})\mathrm{P}(\mu\text{-N}^t\mathrm{Bu})_2\mathrm{P}(\mathrm{N}^t\mathrm{Bu})\mathrm{Te}]_2^{2-}$ with a planar PTeTeP conformation and, subsequently, the cyclic tritelluride $[(^t\mathrm{BuN})\mathrm{P}(\mu\text{-N}^t\mathrm{Bu})_2\mathrm{P}(\mathrm{N}^t\mathrm{Bu})(\mu\text{-TeTeTe})]$.

In their pioneering studies of inorganic macrocycles that incorporate P_2N_2 rings,[1] Wright and co-workers have employed cyclocondensation to generate NH- or O-bridged systems of various sizes involving $\mathrm{P^{III}}_2\mathrm{N}_2$ rings[2,3] and a reductive method for the synthesis of a hexamer in which monoselenido (–Se–) units span $\mathrm{P^{III}P^{V}N_2}$ rings.[4] Recently, we have applied a mild oxidative approach to generate the trimers $[(^t\mathrm{BuN})\mathrm{P}(\mu\text{-N}^t\mathrm{Bu})_2\mathrm{P}(\mathrm{N}^t\mathrm{Bu})(\mu\text{-E–E–})]_3$ with a planar P_6E_6 (E = S, Se) framework in which dichalcogenido (–E–E–) groups are linked by perpendicular $\mathrm{P^{V}}_2\mathrm{N}_2$ rings.[5] The synthesis of these polychalcogen macrocycles involves the two-electron oxidation of the dianions **1a** and **1b** with I_2. We now report a detailed investigation of the oxidation of the tellurium analogue **1c** that provides important insights into the initial oxidation process, as well as a notable difference in the final outcome of the oxidation compared to that observed for **1a** and **1b**. Specifically, we have identified and structurally characterised (a) the dianionic ditelluride $[\mathrm{Te}(^t\mathrm{BuN})\mathrm{P}(\mu\text{-N}^t\mathrm{Bu})_2\mathrm{P}(\mathrm{N}^t\mathrm{Bu})\mathrm{Te}]_2^{2-}$ (**2**), with an unusual planar conformation, as the product of one-electron oxidation of **1c** and (b) the cyclic tritelluride $[(^t\mathrm{BuN})\mathrm{P}(\mu\text{-N}^t\mathrm{Bu})_2\mathrm{P}(\mathrm{N}^t\mathrm{Bu})(\mu\text{-TeTeTe})]$ **(3)** as the result of further oxidation. DFT calculations were carried out in order to determine the reason(s) for the unusual planarity of the PTeTeP unit in the ditelluride **2**.

The oxidation of the dianion **1c** (as its dilithium derivative)[6a] with a one-half molar equivalent of I_2 led to the isolation of extremely sensitive black crystals, which were identified by X-ray crystallography as $[\mathrm{Li(tmeda)}]_2$**2** (Eq. 1).[7] As depicted in Fig. 1, the dianion $[\mathrm{Te}(^t\mathrm{BuN})\mathrm{P}(\mu\text{-N}^t\mathrm{Bu})_2\mathrm{P}(\mathrm{N}^t\mathrm{Bu})\mathrm{Te}]_2^{2-}$ (**2**) is comprised of a central ditellurido unit that links two $\mathrm{P^{V}}_2\mathrm{N}_2$ rings, each of which has exocyclic Te and $\mathrm{N}^t\mathrm{Bu}$ substituents that are *N,Te*- chelated to the tmeda-solvated Li^+ counterions. The $^{31}\mathrm{P}$ NMR spectrum of $[\mathrm{Li(tmeda)}]_2$**2** in d_8-toluene exhibits singlets at $\delta = -78.5$ and -117.0 with $^1J(\mathrm{P,Te}) = 1670$ and 1219 Hz, respectively, reflecting the disparity in the P–Te bond lengths [d(P2–Te2)= 2.396(2) and d(P1–Te1) = 2.497(2) Å]. The Te1–Te1' bond length in **2** is 2.777(3) Å, cf. 2.70-2.71 Å for typical aryl ditellurides,[8] 2.75-2.76 Å for ditellurides supported by an intramolecular Te⋯N interaction,[9] and 2.77 Å for the bulky derivative $(\mathrm{TpsiTe})_2$ (Tpsi = tris(phenyldimethylsilyl)methyl.[10]



1a (E = S), **1b** (E = Se)
1c (E = Te)

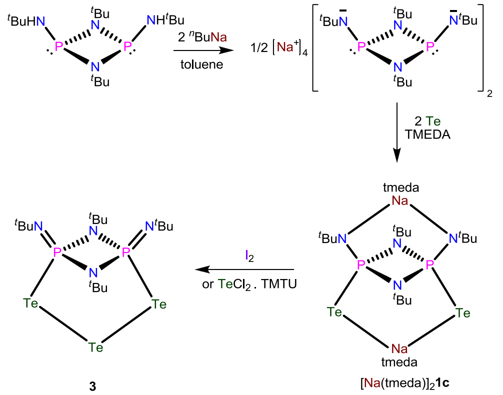


2

Atypically, the ditelluride $[\mathrm{Li(tmeda)}]_2$**2** is perfectly planar (< P–Te–Te–P = 180.0°). The only other examples of antiperiplanar ditellurides are bis(chloro-2-pyridyl) ditelluride[11] and the diacyl ditelluride $(2\text{-MeOC}_6\mathrm{H}_4\mathrm{COTe})_2$,[12] which exhibit intramolecular heteroatom-tellurium interactions and $(\mathrm{TpsiTe})_2$ for which the antiperiplanar conformation is imposed by the bulky substituents.[10] The Te1⋯Te2' distance in $[\mathrm{Li(tmeda)}]_2$**2** (3.884 Å) is shorter than the sum of van der Waals radii for Te (4.12 Å).[13] Moreover, the closely related neutral ditelluride $[(^t\mathrm{BuNH})\mathrm{P}(\mu\text{-N}^t\mathrm{Bu})_2\mathrm{P}(\mathrm{N}^t\mathrm{Bu})\mathrm{Te}]_2$ (**4**), which has a similar steric environment for the Te–Te linkage, exhibits a dihedral angle of −123.8° and a Te–Te bond length of 2.7204(9) Å (Fig. S1).[14] In view of these observations, DFT calculations were carried out to probe whether the conformation of $[\mathrm{Li(tmeda)}]_2$**2** is stabilized by intramolecular Te1⋯Te2' secondary bonding interactions (3.884 Å). Satisfactory structures were obtained from geometry optimizations (PBE-D3, TZP, ZORA) for planar and synclinal models of $[\mathrm{Li(tmeda)}]_2$**2** and **4** simplified using Me groups in lieu of ^{t}Bu. In both instances the planar conformations were higher in energy, by 8 and 37 kJ mol^{-1} for the models of $[\mathrm{Li(tmeda)}]_2$**2** and **4**, respectively. Preferred P–Te–Te–P torsion angles are 98° for the former and 90° for the latter. The small difference of energy suggests that the conformation observed in the crystal structure of $[\mathrm{Li(tmeda)}]_2$**2** is imposed by packing forces. Further analysis on the electronic structures of the $[\mathrm{Li(tmeda)}]_2$**2** models failed to identify a particular orbital interaction or contribution from dispersion that would help stabilize the antiperiplanar geometry.

$$2[\mathrm{Li(tmeda)}]_2\mathbf{1c} \xrightarrow[-2\,\mathrm{LiI}]{\mathrm{I}_2} [\mathrm{Li(tmeda)}]_2\mathbf{2} \qquad (1)$$

In order to provide a direct comparison of the oxidation of **1c** with that of **1a** and **1b**[5], we have developed a synthesis of the sodium salt $[\mathrm{Na(tmeda)}]_2$**1c** via the metallation-telluration sequence illustrated in Scheme 1. Yellow crystals of $[\mathrm{Na(tmeda)}]_2$**1c** suitable for an X-ray analysis were obtained from *n*-hexane at −30 °C and the molecular structure is illustrated in Fig. 2.[15] In contrast to the lithium analogue $[\mathrm{Li(thf)}]_2$**1c** in which the dianionic ligand is coordinated to the Li$^+$ cations asymmetrically (*Te,Te′* and *N,Te* chelation),[6a] the sodium salt $[\mathrm{Na(tmeda)}]_2$**1c** adopts a symmetrical structure (*Te,Te′* and *N,N′* coordination).[17] The mean P–Te distance of 2.420(2) Å in $[\mathrm{Na(tmeda)}]_2$**1c** is shorter by ca. 0.03 Å than that involving the two-coordinate Te in $[\mathrm{Li(thf)}]_2$**1c**.[6a] Consistently, the ^1J(P,Te) coupling constant of 1583 Hz for $[\mathrm{Na(tmeda)}]_2$**1c** is substantially larger than the values of 1309 and 1467 Hz found for the lithium analogue.[6a] A doublet is observed in the ^{125}Te NMR spectrum of $[\mathrm{Na(tmeda)}]_2$**1c** at −148.7 ppm, *cf.* −289 and −87 ppm for the inequivalent Te environments in $[\mathrm{Li(thf)}]_2$**1c**.[6a]



Scheme 1 Synthesis of the cyclic tritelluride **3**

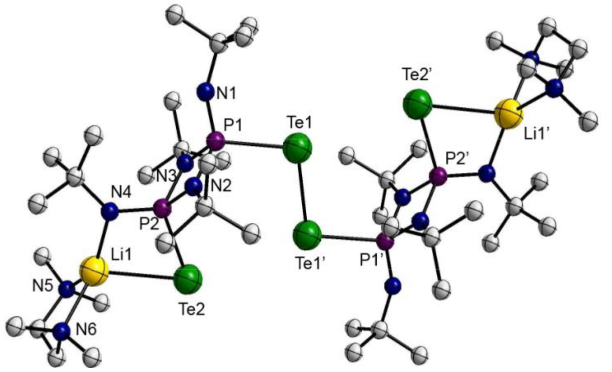


Fig. 1. Molecular structure of $[\mathrm{Li(tmeda)}]_2$**2**. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Te1–Te1′ 2.7768(8), Te1–P1 2.4970(18), Te2–P2 2.3957(18), N4–Li1 2.008(9), Te2–Li1 2.848(12), P1–N1 1.510(6), P2–N4 1.566(5), P–N$_{\mathrm{bridging}}$(range) 1.679(4)-1.712(4), N5–Li1 2.171(9), P1–Te1–Te1’ 104.41(4).

Treatment of $[\mathrm{Na(tmeda)}]_2$**1c** with an equimolar quantity of I$_2$ in toluene produced a dark red-black solid, which was recrystallised from pentane to give black crystals that were identified as the tritelluride $[(^t\mathrm{BuN})\mathrm{P}(\mu\text{-N}^t\mathrm{Bu})_2\mathrm{P}(\mathrm{N}^t\mathrm{Bu})(\mu\text{-TeTeTe})]$ (**3**) by single-crystal X-ray analysis.[18] Higher yields (41 %) of **3** are obtained via metathesis of $[\mathrm{Na(tmeda)}]_2$**1c** with TeCl$_2$·tmtu in toluene (Scheme 1).

As shown in Fig. 3, the molecular structure of **3** is comprised of a tritelluride ligand bridging the P$^{\mathrm{V}}_2$N$_2$ ring. Compound **3** is a rare example of a cyclic tritelluride, the only other representative being the Sn$^{\mathrm{IV}}$ complex [ArSn(μ-Te)$_2$(μ-TeTeTe)SnAr] (Ar = 2,6-bis(2,4,6-triisopropylphenyl)phenyl).[19] Structurally characterised acyclic tritellurides incorporate either bulky substituents RTeTeTeR (R = C(SiMe$_3$)$_3$)[20] or intramolecular N···Te coordination (2-pyridyl-C$_6$H$_5$,[21] 8-Me$_2$NC$_{10}$H$_7$[22]); the thermally unstable dication $[^t\mathrm{Bu}_3\mathrm{PTeTeTeP}^t\mathrm{Bu}_3]^{2+}$ has also been identified.[23] The mean Te–Te bond length of 2.716(1) Å and Te–Te–Te bond angle of 104.50(1)° in **3** are comparable to the corresponding values of 2.705(2) Å and 104.02(5)° found for [ArSn(μ-Te)$_2$(μ-TeTeTe)SnAr].[19] The P–Te bond length of 2.536(1) Å is notably longer (by ca. 0.12 Å) than the mean value for $[\mathrm{Na(tmeda)}]_2$**1c** indicating a weak P–Te bond in **3**. Consistently, the ^1J(P,Te) coupling of 1030 Hz observed in both

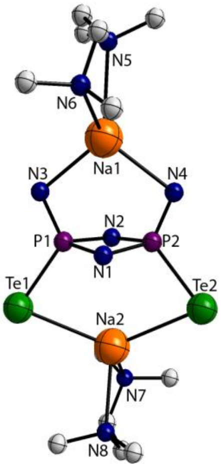


Fig. 2. Molecular structure of $[\mathrm{Na(tmeda)}]_2$**1c.** *tert*-Butyl groups and hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): P1–Te1 2.418(2), P2–Te2 2.422(2), Na1–Te1 3.047(4), Na2–Te2 3.049(3), Na–N (range) 2.451(8)–2.750(9), P1–N3 1.576(7), P2–N4 1.566(7), P–N$_{\mathrm{bridging}}$(range) 1.697(7)–1.719(7); P1–Te1–Na2 80.41(8), P2–Te2–Na2 80.35(8), Te1–Na2–Te2 125.1 (1), N3–Na1–N4 101.2(2), N5–Na1–N6 72.6(3), N7–Na2–N8 76.5(3).

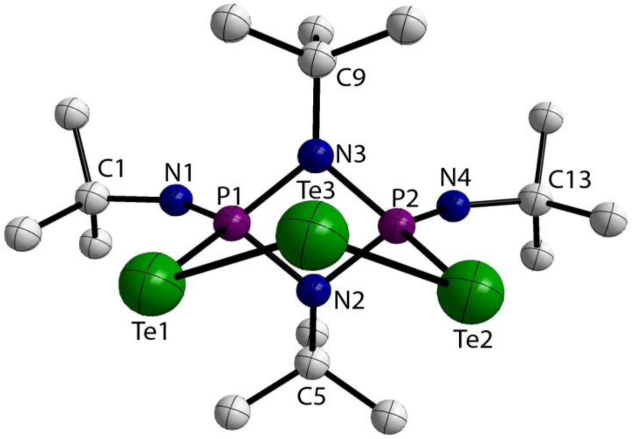


Fig. 3. Molecular structure of **3.** Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): P1–Te1 2.5317(10), P2–Te2 2.5405(10), Te1–Te3 2.7155(4), Te2–Te3 2.7158(4), P1–N1 1.508(3), P2–N4 1.507(4), P–N$_{\mathrm{bridging}}$ 1.679(3)–1.694(3); P1–Te1–Te3 95.63(2), P2–Te2–Te3 96.06(3), Te1–Te3–Te2 104.50(1).

the ^{31}P and ^{125}Te NMR spectra of **3** in d_8-toluene is among the lowest reported for P–Te compounds.[24] The ^{125}Te NMR spectrum of **3** is comprised of a well-separated pseudo-doublet of doublets at −442.8 ppm (^{1}J(P,Te) = 1031 Hz, ^{3}J(P,Te) = 41 Hz), and a pseudo-triplet centred at +361.9 (t, ^{2}J(P,Te) = 35 Hz); these resonances are assigned to the equivalent pair of tellurium atoms Te1, Te2 and the unique tellurium centre Te3, respectively (Fig. 3). The heterocycle **3** is the first structurally characterised neutral P–Te ring, although the cation $[N(P^iPr_2Te)_2]^+$ embodying a five-membered $NP^V{}_2Te_2$ ring is known.[25]

In summary, the formation of the ditellurido linkage in **2** is comparable to the generation of neutral dichalcogenides upon one-electron oxidation of the PNP-bridged monoanions $[EPR_2NPR_2PE]^-$ (E = S, Se, Te; R = ^{i}Pr, ^{t}Bu).[26] The identification of the acyclic intermediate **2** provides an important discernment into the process involved in the construction of $P^V{}_2N_2$-bridged polychalcogen macrocycles via the oxidation pathway.[27] It also supplies an incentive for investigations of the sulfur and selenium analogues, which are potentially versatile building blocks for the construction of $P^V{}_2N_2$-stabilised macrocycles that incorporate main group elements or transition metals in addition to dichalcogenido linkages.

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[†] Electronic supplementary information (ESI) available: Experimental and crystallographic data in pdf format. CCDC references numbers 909218-909222 for ([Na(tmeda)]$_2$**1c**), ([Li(tmeda)]$_2$**2**), **3, 4** and $[Na_4(P_2(\mu\text{-}N^tBu)_2(N^tBu)_2)_2]$

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15. Crystal data for [Na(tmeda)]$_2$**1c**: $C_{28}H_{68}N_8P_2Te_2Na_2$, M = 880.02, monoclinic, space group $P21/n$, a = 11.1830(5), b = 30.2640(12), c = 12.5750(5) Å, $\alpha = \gamma$ = 90.00, β = 95.151(1)°, V = 4238.7(3) Å^3, Z = 4, ρ_{calcd} = 1.379 g cm^{-3}, μ = 1.500 mm^{-1}, T = 173(2) K, 12267 reflections collected (θ range 1.4–27.5°), 7193 unique (R_{int} = 0.0436), R_1 = 0.0644 for 6017 reflections with $I > 2\sigma(I)$] and wR_2 =0.1771(for all data).
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