A planar dianionic ditelluride and a cyclic tritelluride supported by P$_2$N$_2$ rings†

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In their pioneering studies of inorganic macrocycles that incorporate P$_2$N$_2$ rings,1 Wright and co-workers have employed cyclocondensation to generate NH- or O-bridged systems of various sizes involving P$_{10}$N$_2$ rings.2,3 and a reductive method for the synthesis of a hexamer in which monoselenido (TpsiTe) rings, each of which has exocyclic Te and N heteroatoms, are linked by a P$^{III}$N$_2$ ring.4 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 [Te(BuN)P(N'-N'Bu)P(N'Bu)Te]$^{2-}$ (2), with an unusual planar conformation, as its dilithium derivative (TpsiTe) as the product of one-electron oxidation of 1c and (b) the cyclic tritelluride [Te(BuN)P(N'-N'Bu)P(N'Bu)(μ-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 lithium derivative)5a 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 [Li(tmeda)]$_2$ (Eq. 1).7 As depicted in Fig. 1, the dianion [Te(BuN)P(N'-N'Bu)P(N'Bu)Te]$^{2-}$ (2) is comprised of a central ditelluride unit that links two P$_{10}$N$_2$ rings, each of which has exocyclic Te and N'Bu substituents that are N,Te- chelated to the tmeda-solvated Li$^+$ cation. The $^{31}$P NMR spectrum of [Li(tmeda)]$_2$ in $d_6$-toluene exhibits singlets at $\delta = -78.5$ and $-117.0$ with $^3$(P,Te) = 1670 and 1219 Hz, respectively, reflecting the disparity in the P–Te bond lengths (d[P2–Te]= 2.396(2) and d[P1–Te]= 2.497(2) Å). The Te1–Te1’ bond length in 2 is 2.77(3) Å, cf. 2.70–2.76 Å for typical aryl ditellurides,5c 2.75–2.76 Å for ditellurides supported by an intramolecular Te···N interaction,9 and 2.77 Å for the bulky derivative (TpsiTe)$_2$ (Tpsi = tris(phenyl(dimethyl)silyl)methyl).10

Atypically, the ditelluride [Li(tmeda)]$_2$ 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-MeOC$_6$H$_4$COTe)$_2$,12 which exhibit intramolecular heteroatom-tellurium interactions and (TpsiTe)$_2$ for which the antiperiplanar conformation is imposed by the bulky substituents.10 The Te1···Te2’ distance in [Li(tmeda)]$_2$ (3.88 Å) is shorter than the sum of van der Waals radii for Te (4.12 Å).13 Moreover, the closely related neutral ditelluride [(BuNH)P(N'-N'Bu)P(N'Bu)Te]$_2$ (4), which has a similar steric environment for the Te–Te linkage, exhibits a dihedral angle of $-123.8^\circ$ 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 [Li(tmeda)]$_2$ is stabilized by intramolecular Te1···Te2’ secondary bonding interactions (3.88 Å). Satisfactory structures were obtained from geometry optimizations (PBE-D3, TZP, ZORA) for planar and synclinal models of [Li(tmeda)]$_2$ and 4 simplified using Me groups in lieu of Bu. In both instances the planar conformations were higher in energy, by 8 and 37 kJ mol$^{-1}$ for the models of [Li(tmeda)]$_2$ 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 seems to reflect that the conformation observed in the crystal structure of [Li(tmeda)]$_2$ is imposed by packing forces. Further analysis on the electronic structures of the [Li(tmeda)]$_2$ models failed to identify a particular orbital interaction or contribution from dispersion that would help stabilize the antiperiplanar geometry.

**Scheme 1**

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

Treatment of [Na(tmeda)]Ic with an equimolar quantity of I₂ in toluene produced a dark-red-black solid, which was recrystallised from pentane to give black crystals that were identified as the tellurilide [(BuN)P(N−Bu)₃P(N₃Bu)(μ−TeTeTe)] (3) by single-crystal X-ray analysis. Higher yields (41%) of 3 are obtained via metathesis of [Na(tmeda)]Ic with TeCl₄•tmtu in toluene (Scheme 1).

As shown in Fig. 3, the molecular structure of 3 is comprised of a tritelluride ligand bridging the P⁵⁻N₂ ring. Compound 3 is a rare example of a cyclic tellurilide, the only other representative being the Sn⁵⁻ complex [ArSn(μ−Te)(μ−TeTeTe)SnAr] (Ar = 2,6-bis(2,4,6-trisopropylphenyl)phenyl). Structurally characterised acyclic tellurilides incorporate either bulky substituents RTeTeTeR (R = C(SiMe₃)₃) or intramolecular N⋯Te coordination (2-pyridyl-C₆H₄; 8-Me₂NC₆H₅); the thermally unstable dication [Bu₄PbTeTePb₄Bu]⁺ has also been identified. 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)(μ−TeTeTe)SnAr]. The P–Te bond length of 2.536(1) Å is notably longer (by ca. 0.12 Å) than the mean value for [Na(tmeda)]Ic indicating a weak P–Te bond in 3. Consistently, the J(P,Te) coupling of 1030 Hz observed in both

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Fig. 1. Molecular structure of [Li(tmeda)]Ic. 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–Li2 2.848(12), P1–N1 1.510(6), P2–N4 1.566(5), P–N(4sing) (range) 1.679(4)–1.712(4), N5–Li1 2.171(9), P1–Te1–Te1’ 104.41(4).

Fig. 2. Molecular structure of [Na(tmeda)]Ic. 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(4sing) (range) 1.697(7)–1.719(7); P1–Te1–Na2 80.41(8), P2–Te2–Na2 80.35(8), Te1–Na1–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(4sing) 1.679(3)–1.694(3); P1–Te1–Te3 95.63(2), P2–Te2–Te3 96.06(3), Te1–Te3–Te1’ 104.50(1).
the $^{31}$P and $^{125}$Te NMR spectra of 3 in $d_2$-toluene is among the lowest reported for P–Te compounds. The $^{125}$Te NMR spectrum of 3 is comprised of a well-separated pseudo-doubt doublets at $-442.8$ ppm ($J$(P,Te) = 1031 Hz, $J$(P,Te) = 41 Hz), and a pseudo-triplet centred at +361.9 (t, $J$(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(Pr)Te]$_2$]$^+$ embodying a five-membered N$_2$P$_2$Te$_2$ ring is known.25

In summary, the formation of the ditellurido linkage in 2 is comparable to the generation of neutral dithiocagenides upon one-electron oxidation of the PNP-bridged monoanions [EPR$_n$NP$_n$PE] (E = S, Se, Te; R = $^3$Pr, $^3$Bu).26 The identification of the acyclic intermediate 2 provides an important discernment into the process involved in the construction of P$_3$N$_2$-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$_3$N$_2$-stabilised macrocycles that incorporate main group elements or transition metals in addition to dithiocagenido linkages.

### Notes and references

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28 Electronic supplementary information (ESI) available: Experimental and crystallographic data in pdf format. CCDC references numbers 909218-909222 for ([Na(tmeda)]$_2$)[E], ([Li(tmeda)]$_2$)2, 3, 4 and [Na$_2$(μ-N$_2$Bu)(N$_2$Bu)$_2$]3.


7. Crystal data for [Li(tmeda)]$_2$: Cs$_2$H$_2$N$_2$P$_3$Te$_2$, $M$ = 1818.12, triclinic, space group $P1$, $a$ = 13.760(3), $b$ = 14.301(3), $c$ = 14.481(3), $\alpha$ = 60.533(5), $\beta$ = 65.043(5), $\gamma$ = 72.923, monoclinic, space group $I2$/$a$, $a$ = 14.2630(3), $b$ = 11.5420(3), $c$ = 9.00, $\beta$ = 95.1511(5), $V$ = 4238.7(3) Å$^3$, $Z$ = 4, $\rho_{calcd}$ = 1.397 g cm$^{-3}$, $\mu$ = 1.500 mm$^{-1}$, $Tm$ = 173(2) K, 12267 reflections collected ($\theta$ 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).

8. The new reagent [Na$_2$(μ-N$_2$Bu)(P$_2$N$_2$Bu)$_2$]$_2$ was shown to be a dimer by a single-crystal X-ray structural determination (see ESI).


10. Crystal data for 3: Cs$_2$H$_2$N$_2$P$_3$Te$_2$, $M$ = 729.23, monoclinic, space group $C2/c$, $a$ = 33.1490(2), $b$ = 14.2630(3), $c$ = 11.5420(3), $\alpha$ = $\gamma$ = 90.00, $\beta$ = 107.354(5), $V$ = 5208.7(2) Å$^3$, $Z$ = 8, $\rho_{calcd}$ = 1.860 g cm$^{-3}$, $\mu$ = 3.469 mm$^{-1}$, $Tm$ = 173(2) K, 20105 reflections collected ($\theta$ range 1.6–27.4°), 5894 unique ($R_{int}$ = 0.0408), $R_1$ = 0.0358 for 5360 reflections with $I > 2\sigma(I)$ and $wR_2$ = 0.0742 (for all data).


