

# The cyclic $[\text{N}(\text{P}^i\text{Pr}_2\text{E})_2]^+$ ( $\text{E} = \text{Se}, \text{Te}$ ) cations: a new class of inorganic ring system

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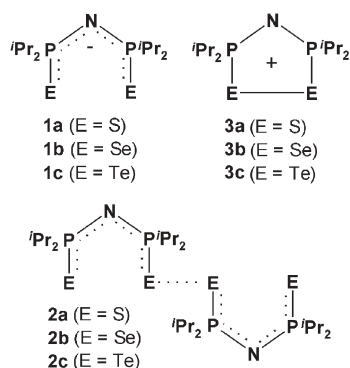
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The two-electron oxidation of  $[(\text{tmeda})\text{NaN}(\text{P}^i\text{Pr}_2\text{E})_2]$  with iodine produces the cyclic  $[\text{N}(\text{P}^i\text{Pr}_2\text{E})_2]^+$  ( $\text{E} = \text{Se}, \text{Te}$ ) cations, which exhibit long E–E bonds in the iodide salts.

The coordination chemistry of the dichalcogenoimidodiphosphinate ligands  $[\text{N}(\text{PR}_2\text{E})_2]^-$  **1** ( $\text{E} = \text{O}, \text{S}, \text{Se}$ ) has been studied extensively.<sup>1</sup> This pervasive interest arises from a number of potential uses *e.g.*, as lanthanide shift reagents,<sup>2</sup> in luminescent materials,<sup>3</sup> or in metal extraction processes.<sup>4</sup> More recently, O'Brien and co-workers have shown that certain metal complexes of the isopropyl derivatives **1a** and **1b** are sufficiently volatile to serve as single-source precursors for the production of thin semi-conducting films.<sup>5</sup> The cadmium complex of **1b** produces CdSe quantum dots in a solvothermal reaction.<sup>6</sup>



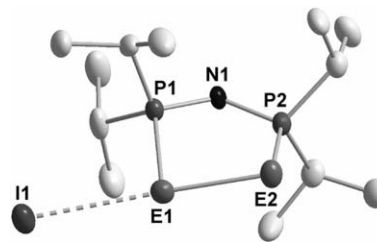
The neutral precursors to the anionic ligands **1a** and **1b** are readily made by direct reaction between  $\text{HN}(\text{P}^i\text{Pr}_2)_2$  and elemental sulfur or selenium, respectively,<sup>7</sup> but this reaction is not successful for the synthesis of  $\text{HN}(\text{P}^i\text{Pr}_2)_2$ . Consequently, we have developed a different approach to the synthesis of the anionic tellurium ligands  $[\text{N}(\text{PR}_2\text{Te})_2]^-$  ( $\text{R} = ^i\text{Pr}, \text{Ph}$ ) that involves metallation of  $\text{HN}(\text{PR}_2)_2$  with NaH prior to reaction with tellurium.<sup>8,9</sup> A fascinating feature of the chemistry of **1c** is the formation of the unusual ditelluride **2c** upon stoichiometric oxidation of the sodium salt with iodine.<sup>8,9</sup> The ditelluride **2c** may be considered to be the dimer of the tellurium-centered radical  $[\text{TeP}^i\text{Pr}_2\text{N}^i\text{Pr}_2\text{P}^i\text{Te}]^{\cdot}$ .<sup>9,10</sup> The discovery of **2b**<sup>10</sup> and **2c**<sup>9</sup> poses the intriguing question of whether the corresponding cations **3b** and **3c** can be prepared, thus completing the sequence of different oxidation states ( $-1, 0, +1$ ) for the dichalcogenoimidodiphosphinate ligand system. In this

communication we describe the synthesis, molecular and electronic structures of the salts  $[\text{N}(\text{P}^i\text{Pr}_2\text{Se})_2]\text{I}$  (**4**) and  $[\text{N}(\text{P}^i\text{Pr}_2\text{Te})_2]\text{I}$  (**5**), which contain the cyclic cations **3b** and **3c**, respectively. These formally  $6\pi$ -electron cations represent a novel class of inorganic ring system<sup>11</sup> and provide a new feature of the chemistry of dichalcogenoimidodiphosphinates.

The cations **3b** and **3c** are readily generated by stoichiometric oxidation of either the corresponding anions **1b** and **1c** or, in the case of **3c**, the neutral dichalcogenide **2c** with iodine. Thus the reactions of  $[(\text{tmeda})\text{NaN}(\text{P}^i\text{Pr}_2\text{E})_2]$  ( $\text{E} = \text{Se}, \text{Te}$ ) with one equivalent of  $\text{I}_2$  at  $-78^\circ\text{C}$  produce the iodide salts **4** and **5** in 90 and 92% yields, respectively.<sup>†</sup> The surprisingly air-stable compounds<sup>13</sup> were characterized in the solid state by X-ray crystallography<sup>‡</sup> and in solution by multinuclear NMR spectroscopy.

X-Ray crystallographic analyses revealed that **4** and **5** are comprised of five-membered  $[\text{NP}_2\text{E}_2]^+$  cations and an iodide counterion that interacts with one of the chalcogen atoms of the cation resulting in inequivalent  $^i\text{Pr}_2\text{P}$ -units.

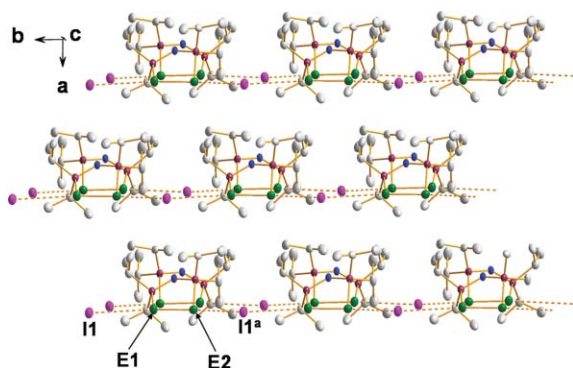
The molecular structure (Fig. 1) and crystal packing (Fig. 2) are essentially the same for **4** and **5**. The compounds form infinite chains of non-planar five-membered rings linked by chalcogen–iodine interactions. The two  $\text{E}\cdots\text{I}$  interactions show only a slight variation in **5** (3.430(1) and 3.494(1) Å), whereas the corresponding difference is more pronounced in **4** (3.150(1) and 4.006(1) Å). The  $\text{Te}\cdots\text{I}$  contacts in **5** are comparable to the ionic interactions found in  $\text{Et}_3\text{Te}^+\cdots\text{I}^-$  (3.418 Å)<sup>14</sup> and in  $\{[(^i\text{BuNH})\text{Te}^+(\mu\text{-N}^i\text{Bu})_2\text{Te}(\mu\text{-O})_2]_2\}\cdots(\text{I}^-)_2$  (3.410(1) and 3.445(1) Å).<sup>15</sup> The shorter  $\text{Se}\cdots\text{I}$  interaction in **4** is somewhat longer than that observed in  $\text{Ph}_2\text{Se}_2\text{I}_2$



**Fig. 1** Molecular structures of **4** ( $\text{E} = \text{Se}$ ) and **5** ( $\text{E} = \text{Te}$ ). Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level using the structure **4**. Selected bond distances (Å) and angles ( $^\circ$ ) [calculated values are given in brackets]. **4**:  $\text{Se2-P2}$  2.229(2) [2.222],  $\text{P2-N1}$  1.590(5) [1.618],  $\text{P1-N1}$  1.593(5) [1.625],  $\text{Se1-P1}$  2.273(2) [2.283],  $\text{Se1-Se2}$  2.484(1) [2.595],  $\text{Se1}\cdots\text{I1}$  3.150(1),  $\text{P1-N1-P2}$  128.3(4) [125.7],  $[\text{N-P-Se}]$  108.6 [110.2],  $\tau$   $\text{P1-Se1-Se2-P2}$   $-25.05(7)$  [ $-28.6$ ]. **5**:  $\text{Te2-P2}$  2.437(3) [2.449],  $\text{P2-N1}$  1.552(6) [1.616],  $\text{P1-N1}$  1.621(6) [1.626],  $\text{Te1-P1}$  2.396(3) [2.496],  $\text{Te1-Te2}$  2.840(1) [2.884],  $\text{Te1}\cdots\text{I1}$  3.430(1),  $\text{P1-N1-P2}$  133.5(4) [129.5],  $[\text{N-P-Te}]$  109.4 [111.2],  $\tau$   $\text{P1-Te1-Te2-P2}$   $-25.84(7)$  [ $-27.2$ ].

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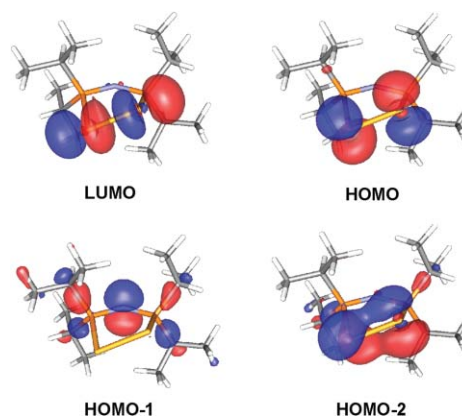


**Fig. 2** Crystal packing in **4** (E = Se) and **5** (E = Te). Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level using the structure **4**. E...I close contacts: Se2...I1<sup>a</sup> 4.006(1) Å and Te2...I1 3.494(1) Å. Symmetry coordinates:  $x, y - 1, z$ .

(2.992 Å),<sup>16,17</sup> which also contains a Se–Se...I-unit. The second Se...I interaction is close to the sum of van der Waals radii for selenium and iodine (4.15 Å).<sup>18</sup>

In contrast to the planarity of related chalcogen–nitrogen cations [RCN<sub>2</sub>E<sub>2</sub>]<sup>+</sup> (E = S, Se),<sup>19</sup> [E<sub>3</sub>N<sub>2</sub>]<sup>2+</sup> (E = S, Se),<sup>20</sup> and the nitrogen-rich system [S<sub>2</sub>N<sub>3</sub>]<sup>+</sup>,<sup>21</sup> the five-membered ring in **4** and **5** is distinctly puckered (Fig. 1). The mean N–P–E bond angles (108.6° in **4** and 109.4° in **5**) are close to the ideal tetrahedral values. The P–N–P bond angles are 128.3(4)° and 133.5(4)° in **4** and **5**, respectively. DFT calculations show localization of the positive charge on the phosphorus atoms.<sup>22</sup> However, the average P–N bond lengths (1.592 Å in **4** and 1.587 Å in **5**) are not significantly different from the mean value observed for **2c**.<sup>9</sup> The chalcogen–iodine interactions cause a significant perturbation of the P–E bonds (P–Se: 2.229(2) and 2.273(2) Å in **4**; P–Te: 2.396(3) and 2.437(3) Å in **5**, *cf.* 2.394(2) and 2.489(2) Å in the neutral ligand **2c**). The most interesting structural features of **4** and **5** are the long E–E bond lengths (2.484(1) Å in **4** and 2.840(1) Å in **5**), which are *ca.* 0.14 and 0.10 Å longer than the Se–Se and Te–Te single-bond values.<sup>26</sup> For comparison, the Se–Se bond lengths in the six  $\pi$ -electron, five-membered cyclic cations in the salts [PhCN<sub>2</sub>Se<sub>2</sub>][PF<sub>6</sub>]<sup>27</sup> and [Se<sub>3</sub>N<sub>2</sub>][AsF<sub>6</sub>]<sup>20</sup> are 2.260(5) and 2.334(3) Å, respectively. The Te–Te bond length in the cation [(Te<sub>2</sub>SN<sub>2</sub>)Cl]<sup>+</sup>, in which one of the Te atoms is three-coordinate, is 2.731(2) Å.<sup>28,29</sup>

DFT calculations have provided important insights into the electronic structures in the cyclic cations **3b** and **3c**.<sup>22</sup> The calculated bond parameters for **4** and **5** are in reasonable agreement with the observed structural parameters (see caption to Fig. 1). The differences in the optimized geometries compared to the observed structures are attributed primarily to the molecular packing interactions observed in the solid state. The three highest occupied molecular orbitals in the five-membered rings **3**, illustrated in Fig. 3, are  $\pi$ -type orbitals. Thus, although they are non-planar, the cyclic cations are formally six  $\pi$ -electron systems. The  $\pi$ -bond order is low, however, since the bonding effect of the E–E  $\pi$ -bonding orbital (HOMO-2) is essentially cancelled by the double occupation of the E–E  $\pi^*$ -antibonding orbital (HOMO) and the third occupied  $\pi$ -orbital is a primarily non-bonding nitrogen-centered orbital (HOMO-1). The long chalcogen–chalcogen bonds in **4** and **5** are attributed to the donation of electron density from a lone pair on the iodide counterion into the  $\sigma^*$  orbital (LUMO), *cf.* the formation of the triiodide I<sub>3</sub><sup>−</sup> anion from



**Fig. 3** Frontier orbitals in the [N(P'Pr<sub>2</sub>E)<sub>2</sub>]<sup>+</sup> (E = Se, Te) rings.

an I<sup>−</sup> ion and an I–I molecule.<sup>30,31</sup> DFT calculations confirm this view of the E...I interaction. The calculated Te–Te bond lengths for Te...I separations of 3.5, 4.0 and 4.5 Å are 2.880, 2.795 and 2.720 Å, respectively.

The <sup>31</sup>P{<sup>1</sup>H} NMR spectra of **4** and **5** exhibit singlets at 92.8 and 68.1 ppm, respectively, with chalcogen satellites arising from an AA'X spin system of magnetically inequivalent phosphorus atoms bonded to chalcogens with low natural abundance of an isotope with nuclear spin 1/2 (A, A' = <sup>31</sup>P; X = <sup>77</sup>Se, <sup>125</sup>Te). The singlets do not resolve into the expected two resonances (mutually coupled doublets) even at −100 °C, indicating that the ionic interaction to one of the chalcogens is insignificant in solution. This is confirmed by the <sup>77</sup>Se NMR spectrum of **4**, which exhibits only one broad doublet at 297 ppm (<sup>1</sup>J<sub>Se,P</sub> ≈ 430 Hz). The <sup>125</sup>Te NMR resonance for **5** could not be observed owing to the low solubility of the compound. The <sup>1</sup>H and the <sup>13</sup>C{<sup>1</sup>H} NMR spectra reveal inequivalent <sup>i</sup>Pr-groups for **4** and **5**. Taken together, the multinuclear NMR data indicate C<sub>2</sub> symmetry for the cationic rings in solution.

In summary, the five-membered cyclic cations **3b** and **3c** are the first examples of cations based on the extensively studied EPNPE (E = S, Se, Te) ligand framework. As such they complete the redox sequence −1/0/+1 for dichalcogenoimidodiphosphinates. Electrochemical studies of these systems and the synthesis of ion-separated salts are in progress.

## Notes and references

† The reagent [N(P'Pr<sub>2</sub>Te)<sub>2</sub>] was prepared by the method described earlier<sup>9</sup> and [(tmeda)NaN(P'Pr<sub>2</sub>E)<sub>2</sub>] (E = Se, Te) were prepared by modifications of the procedure reported for [(tmeda)NaN(PPh<sub>2</sub>Te)<sub>2</sub>].<sup>8</sup>

**4**: A solution of [(tmeda)NaN(P'Pr<sub>2</sub>Se)<sub>2</sub>] (0.273 g, 0.50 mmol) in toluene (30 mL) was cooled to −78 °C and a cold (0 °C) solution of I<sub>2</sub> (0.127 g, 0.50 mmol) in THF (15 mL) was added dropwise *via* cannula. The resulting red solution was stirred for 1 h at −78 °C and for 2 h at room temperature. The solvents were removed under vacuum and the residue was dissolved in toluene and then filtered to remove NaI. Toluene was evaporated under vacuum and the resulting powder was washed with *n*-hexane, affording **4** as a red, microcrystalline powder (0.239 g, 90%). Elemental analysis calcd (%) for C<sub>12</sub>H<sub>28</sub>I<sub>2</sub>N<sub>2</sub>P<sub>2</sub>Se<sub>2</sub>: C 27.03, H 5.29, N 2.63; found: C 27.10, H 5.24, N 2.85%. <sup>1</sup>H NMR (D<sub>8</sub>-THF, 23 °C):  $\delta$  = 2.73 [2 × sept., <sup>3</sup>J(H,H) = 7 Hz, 4H; CH(CH<sub>3</sub>)<sub>2</sub>], 1.37 [dd, <sup>3</sup>J(H,H) = 7 Hz, <sup>3</sup>J(H,P) = 18 Hz, 12H; CH(CH<sub>3</sub>)<sub>2</sub>], 1.35 [dd, <sup>3</sup>J(H,H) = 7 Hz, <sup>3</sup>J(H,P) = 20 Hz, 12H; CH(CH<sub>3</sub>)<sub>2</sub>]; <sup>13</sup>C{<sup>1</sup>H} NMR:  $\delta$  = 33.2 (m, 4C; CH(CH<sub>3</sub>)<sub>2</sub>), 18.6 (s, 4C; CH(CH<sub>3</sub>)<sub>2</sub>), 17.7 (s, 4C; CH(CH<sub>3</sub>)<sub>2</sub>); <sup>31</sup>P{<sup>1</sup>H} NMR:  $\delta$  = 92.8 (s + satellites, <sup>1</sup>J(<sup>77</sup>Se,P) = 440 Hz, <sup>2</sup>J(P,P) = 34 Hz); <sup>77</sup>Se NMR:  $\delta$  = 297 (br, d, <sup>1</sup>J(<sup>77</sup>Se,P) ≈ 430 Hz). Yellow, block-like crystals of **4** were grown from a THF–toluene solution.

**5 from [(tmeda)NaN(P<sup>Pr</sup>Te)<sub>2</sub>]:** The salt **5** was obtained as a dark red, crystalline powder (0.291 g, 92%) from the reaction of [(tmeda)NaN(P<sup>Pr</sup>Te)<sub>2</sub>] (0.321 g, 0.50 mmol) in toluene (30 mL) with I<sub>2</sub> (0.127 g, 0.50 mmol) in THF (15 mL) by using a procedure identical to that described above for **4**. Elemental analysis calcd (%) for C<sub>12</sub>H<sub>28</sub>I<sub>1</sub>N<sub>1</sub>P<sub>2</sub>Te<sub>2</sub>: C 22.86, H 4.48, N 2.22; found: C 22.68, H 4.39, N 2.33%. <sup>1</sup>H NMR (D<sub>8</sub>-THF, 23 °C): δ = 2.62 [2 × sept, <sup>3</sup>J(H,H) = 7 Hz, 4H; CH(CH<sub>3</sub>)<sub>2</sub>], 1.35 [dd, <sup>3</sup>J(H,H) = 7 Hz, <sup>3</sup>J(H,P) = 18 Hz, 12H; CH(CH<sub>3</sub>)<sub>2</sub>], 1.31 [dd, <sup>3</sup>J(H,H) = 7 Hz, <sup>3</sup>J(H,P) = 20 Hz, 12H; CH(CH<sub>3</sub>)<sub>2</sub>]; <sup>13</sup>C{<sup>1</sup>H} NMR: δ = 33.1 (m, 4C; CH(CH<sub>3</sub>)<sub>2</sub>), 19.6 (s, 4C; CH(CH<sub>3</sub>)<sub>2</sub>), 18.1 (br. s, 4C; CH(CH<sub>3</sub>)<sub>2</sub>); <sup>31</sup>P{<sup>1</sup>H} NMR: δ = 68.1 (s + satellites, <sup>1</sup>J(<sup>125</sup>Te,P) = 1040 Hz, <sup>2</sup>J(P,P) = 31 Hz). Dark red, block-like crystals of **5** were grown from a THF–toluene solution.

**5 from 2c:** [N(P<sup>Pr</sup>Te)<sub>2</sub>]<sub>2</sub> (0.100 g, 0.10 mmol) and I<sub>2</sub> (0.026 g, 0.10 mmol) were added to the same flask and then cold (−78 °C) toluene (30 mL) was introduced *via* cannula. The resulting dark red solution was stirred for 1 h at −80 °C and for 2 h at room temperature. The solvent was removed under vacuum, affording **5** as a dark red powder (0.113 g, 90%).

‡ Crystal data for **4**: C<sub>12</sub>H<sub>28</sub>I<sub>1</sub>N<sub>1</sub>P<sub>2</sub>Se<sub>2</sub>, *M<sub>r</sub>* = 533.11, monoclinic, space group *Cc*, *a* = 14.494(3), *b* = 9.592(2), *c* = 14.163(3) Å, β = 105.45(3)°, *V* = 1897.8(7) Å<sup>3</sup>, *Z* = 4, ρ<sub>calcd</sub> = 1.866 g cm<sup>−3</sup>, μ = 5.679 mm<sup>−1</sup>, *T* = 173(2) K, 6209 reflections collected (θ range = 4.23–25.02°), 3258 unique (*R*<sub>int</sub> = 0.0377), *R*<sub>1</sub> = 0.0348 [for 3035 reflections with *I* > 2σ(*I*)] and *wR*<sub>2</sub> = 0.0861 (for all data). Crystal data for **5**: C<sub>12</sub>H<sub>28</sub>I<sub>1</sub>N<sub>1</sub>P<sub>2</sub>Te<sub>2</sub>, *M<sub>r</sub>* = 630.39, monoclinic, space group *Cc*, *a* = 14.187(3), *b* = 9.756(2), *c* = 14.682(3) Å, β = 108.60(3)°, *V* = 1926.0(7) Å<sup>3</sup>, *Z* = 4, ρ<sub>calcd</sub> = 2.174 g cm<sup>−3</sup>, μ = 4.786 mm<sup>−1</sup>, *T* = 173(2) K, 5647 reflections collected (θ range = 2.72–25.02°), 3201 unique (*R*<sub>int</sub> = 0.0391), *R*<sub>1</sub> = 0.0320 [for 2994 reflections with *I* > 2σ(*I*)] and *wR*<sub>2</sub> = 0.0831 (for all data). The structure of **5** was disordered containing two overlapping molecules. In the final refinement the main component was 92% abundant. For the minor 8% component, only the heaviest atoms (I, Te, P) were located from the density Fourier map. The hydrogen atoms were calculated geometrically and were riding on their respective carbon atoms. The structures were solved and refined by using SHELXS-97 and SHELXL-97.<sup>32</sup> CCDC 287969 and 287970. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b600040a

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