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The Cyclic \([\text{N(P}^i\text{Pr}_2\text{E})_2]^+\) \((\text{E} = \text{Se}, \text{Te})\) Cations: A New Class of Inorganic Ring System

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

The coordination chemistry of the dichalcogenimidodiphosphinate ligands \([\text{N(PR}_2\text{E}_2)]\) \((\text{E} = \text{O}, \text{S}, \text{Se})\) has been studied extensively.\(^1\) This pervasive interest arises from a number of potential uses, such as lanthanide shift reagents,\(^2\) in luminescent materials,\(^3\) or in metal extraction processes.\(^4\) More recently, O’Brien and co-workers have shown that certain metal complexes of the isopropyl derivatives \(\text{HN(PR}_2\text{E})\) are readily made by direct reaction between \(\text{HN(PR}_2\text{E})\) and \(\text{NaH}\) prior to reaction with tellurium.\(^5,\)\(^9\) A fascinating feature of the chemistry of \(\text{TeC}\) is the formation of the unusual ditelluride \(\text{TeC}\) on stoichiometric oxidation of the sodium salt with iodine.\(^8,\)\(^9\) The ditelluride \(\text{TeC}\) may be considered to be the dimer of the tellurium-centered radical \(\text{[TePPr}_2\text{N}^i\text{Pr}_2\text{PPr}]}\).\(^9,\)\(^10\) The discovery of \(\text{TeC}\) poses the intriguing question of whether the corresponding cations \(\text{TeC}\) and \(\text{TeC}\) can be prepared, thus completing the sequence of different oxidation states (-1, 0, +1) for the dichalcogenimidodiphosphinate ligand system. In this communication we describe the synthesis, molecular and electronic structures of the salts \([\text{N(P}^i\text{Pr}_2\text{Se})_2\text{I}]\) \((\text{E} = \text{Se})\) and \([\text{N(P}^i\text{Pr}_2\text{Te})_2\text{I}]\) \((\text{E} = \text{Te})\), respectively. These formally 6-electron cations represent a novel class of inorganic ring system\(^11\) and provide a new feature of the chemistry of dichalcogenimidodiphosphinates.

The cations \(\text{TeC}\) and \(\text{TeC}\) are readily generated by stoichiometric oxidation of either the corresponding anions \(\text{TeC}\) and \(\text{TeC}\) or, in the case of \(\text{TeC}\), the neutral dichalcogenide \(\text{TeC}\) with iodine. Thus the reactions of \([\text{tmeda}]\text{NaN}(\text{PPr}_2\text{E}_2)]\) \((\text{E} = \text{Se}, \text{Te})\) with one equivalent of \(\text{I}_2\) at \(-78 \degree\) \(\text{C}\) produce the iodide salts \(\text{TeC}\) and \(\text{TeC}\) in 90 and 92 % yields, respectively.\(^1\) The surprisingly air-stable compounds\(^13\) were characterized by multinuclear NMR spectroscopy and by X-ray crystallography.\(^8\) The NMR spectra reveal inequivalent \(\text{PPr}^2\) units for both compounds. In the \(^1\)H NMR spectra, two sets of doublets of doublets for the Me-groups and two sets of overlapping septets (appearing as an octet) for the CH-hydrogens are observed.\(^6\) Consistently, the \(^1\)C\(^{1}\)H NMR spectra show two singlets for the Me-groups and a multiplet for the \(\alpha\)-carbons of the \(\text{PPr}^2\)-groups arising from an AX\(^2\) spin system.\(^14\) The \(^3\)P\(^{1}\)H NMR spectra of \(\text{TeC}\) and \(\text{TeC}\) exhibit broad singlets at 92.9 and 68.0 ppm, respectively, with broad chalcogen satellites \((J_{\text{ScP}} = 395 \text{ Hz}, J_{\text{TeP}} = 1035 \text{ Hz})\). These broad signals do not resolve into the expected two resonances (mutually coupled doublets) even at \(-60 \degree\) \(\text{C}\) indicating conformational non-rigidity within the rings persists at low temperature. The \(^77\)Se NMR spectrum of \(\text{TeC}\) exhibits a broad doublet at 297 \(\text{ppm}\) \((J_{\text{SeP}} \approx 420 \text{ Hz})\), but the \(^125\)Te NMR resonance for \(\text{TeC}\) could not be observed owing to the low solubility of the compound.

X-ray crystallographic analyses revealed that \(\text{TeC}\) and \(\text{TeC}\) are comprised of five-membered \([\text{NP}^i\text{PR}]\) cations and an iodide counter-ion that interacts with one of the chalcogen atoms of the cation resulting in inequivalent \(\text{PPr}^2\)-units. The molecular structure (Figure 1) and crystal packing (Figure 2) are essentially the same for \(\text{TeC}\) and \(\text{TeC}\). 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 \(\text{TeC}\) (3.430(1) Å and 3.495(1) Å), whereas the corresponding difference is more pronounced in \(\text{TeC}\) (3.150(1) and 4.006(1) Å). The \(\text{Te}\cdots\text{I}\) contacts in \(\text{TeC}\) are comparable to the iodine interactions found in EtTe\(^2\cdots\cdot\text{I}\) (3.418 Å)\(^15\) and in \([\text{EtBuNH}]\text{Te}^2\cdots\text{I}\) (3.410(1) Å and 3.445(1) Å).\(^15\) The shorter \(\text{Se}\cdots\text{I}\) interaction in \(\text{TeC}\) is somewhat longer than that observed in \(\text{Ph}_2\text{SeI}_2\) (2.992 Å), which also contains a Se-Se\cdots\cdot\text{I}-unit. The second Se\cdots\cdot\text{I} interaction is close to the sum of van der Waals radii for selenium and iodine (4.15 Å).\(^18\)

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Figure 1. Molecular structures of 4 (E = Se) and 5 (E = Te). Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at 50% probability level using the structure 4. Selected bond distances (Å) and angles (°) [calculated values are given in brackets]. 4: Se-C2 2.229(2) [2.222], P2-N1 1.590(5) [1.618], P1-N1 1.593(5) [1.625], Se1-P1 2.273(2) [2.283], Se1-Se2 2.484(1) [2.595], Se1···I1 3.150(1), P1-N1-P2 128.3(4) [125.7], N-P-Se 108.6 [110.2], τ P1-Se1-Se2-P2 -25.05(7) [-28.6]. 5: Te2-P2 2.395(3) [2.449], P2-N1 1.553(6) [1.616], P1-N1 1.625(6) [1.626], Te1-P1 2.395(3) [2.496], Te1-Te2 2.839(1) [2.884], Te1···I1 3.430 (1), P1-N1-P2 132.2(4) [129.5], N-P-Te 109.5 [111.2], τ P1-Te1-Te2-P2 -25.84(7) [-27.2].

Figure 2. Figure 2. Crystal packing in 4 (E = Se) and 5 (E = Te). Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at 50% probability level using the structure 4. E···I close contacts: Se2···I1 4.006(1) Å and Te2···I1 3.430 (1), P1-P2 2.850(2) Å, P2-N1 1.590(5) [1.618], P1-N1 1.593(5) [1.625], Se1-P1 2.273(2) [2.283], Se1-Se2 2.484(1) [2.595], Se1···I1 3.150(1), P1-N1-P2 128.3(4) [125.7], N-P-Se 108.6 [110.2], τ P1-Se1-Se2-P2 -25.05(7) [-28.6].

Figure 3. Frontier orbitals in the [Ni(PPr,E)]²⁺ (E = Se, Te) rings. Te-Te bond length in the cation [(Te2Se2)Cl]²⁺, in which one of the Te atoms is three-coordinate, is 2.731(2) Å. 18, 29 DFT calculations have provided important insights into the electronic structures in the cyclic cations 3b and 3c. The calculated bond parameters for 4 and 5 are in reasonable agreement with the observed structural parameters (see caption to Figure 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 Figure 3, are π-type orbitals. Thus, although they are non-planar, the cyclic cations are formally six π-electron systems.

In contrast to the planarity of related chalcogen-nitrogen cations [RCN2E]²⁺ (E = S, Se), [E2N]³⁻ (E = S, Se), and the nitrogen-rich system [S2N]²⁺, the five-membered ring in 4 and 5 is distinctly puckered (Figure 1). The mean N-P-E bond angles (108.6° in 4 and 109.5° in 5) are close to the ideal tetrahedral values. The P-N-P bond angles are 128.3(4)° and 133.2(4)° in 4 and 5, respectively. DFT calculations show localization of the positive charge on the phosphorus atoms. However, the average P-N bond lengths (1.592 Å in 4 and 1.589 Å in 5) are not significantly different from the mean value observed for 2c.9 The chalcogen-nitrogen interactions cause a significant perturbation of the P-E bonds (P-Se: 2.229(2) and 2.273(2) Å in 4; P-Te: 2.395(3) and 2.436(3) Å in 5, cf. 2.394(2) and 2.489(2) Å in the neutral ligand 2c). 10 The most interesting structural features of 4 and 5 are the long E-E bond lengths (2.484(1) Å in 4 and 2.839(1) Å in 5), which are ca. 0.14 and 0.10 Å longer than the Se-Se and Te-Te single-bond values. 11 For comparison, the Se-Se bond lengths in the six π-electron, five-membered cyclic cations in the salts [PhCNSe2][PF6]²⁻ and [Se2N2][AsF6]³⁻ are 2.260(5) and 2.253(3) Å, respectively. The

Notes and references

14 Crystal data for 4: C₆H₅₂[N,P,Se]₂, Mᵣ = 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) Å³, Z = 4, ρcalc = 1.866 g cm⁻³, μ = 5.679 mm⁻¹, T = 173(2) K, 6209 reflections collected (θ range = 4.23-25.02°), 3258 unique (Rint = 0.0377), R = 0.0348 [for 3035 reflections with Dmax(θ)] and wR = 0.0861
15 (for all data). Crystal data for 5: C₆H₅₂[N,P,Se]₂, Mᵣ = 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) Å³, Z = 4, ρcalc = 2.174 g cm⁻³, μ = 4.786 mm⁻¹, T = 173(2) K, 5647 reflections collected (θ range = 4.23-25.02°), 3201 unique (Rint = 0.0391), R = 0.0317 [for 2994 reflections
The structure of 5 was disordered containing two overlapping molecules. In the final refinement the main component was 93% abundant. For the minor 7% component, only the heaviest atoms (I, Te, P) were located from the density Fourier map. All non-hydrogen atoms in 4 and those of the main component in 5, were refined with anisotropic thermal parameters. The hydrogen atoms were calculated geometrically and were riding on their respective carbon atoms. The structures were solved by direct methods using SHELXLS-97 and the model refined by using SHELXL-97.

The reagent [NaP(TeP2)] was prepared by the method described earlier and [tmeda]NaP(TeP3) (E= Se, Te) were prepared by modifications of the procedure reported for [tmeda]NaP(PrP3)Te3].

A solution of [(tmeda)NaP(PrP3)Se2] (0.273 g, 0.50 mmol) in toluene (30 mL) was cooled to -7 °C and a cold (0 °C) solution of I3 (0.127 g, 0.50 mmol) 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 Na+ 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 calcld. (%) for C12H13N2P3Te: C 27.03, H 5.29, N 4.02. M.p. 165 °C; CH2Cl2.

[(tmeda)NaN(P(PrP3)Te3)] crystalline powder (0.291 g, 92%) from the reaction of 

Yellow, block-like crystals of 4 were grown from a THF/toluene solution.

5 from [(tmeda)NaP(PPi)Te3]: The salt 5 was obtained as a dark red, microcrystalline powder (0.291 g, 92%) from the reaction of [(tmeda)NaP(PPi)Te3] (0.321 g, 0.50 mmol) in toluene (30 mL) with I3 (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 affording 5 as a dark red powder (0.113 g, 90%).


Crystalline samples of 4 and 5 remained unchanged after exposure to the atmosphere for several weeks, but decompose slowly in solutions in organic solvents.


Mulliken population analysis shows that a significant portion of the positive charge is localized on the phosphorus atom: P=O 0.3, N 0.2, Se 0.01 in 3b and P 0.3, N -0.29, Te 0.02 in 3c. Computational details: the structures of 3, 4, and 5 were optimized by using DFT and the hybrid PBE0 exchange-correlation functional. The calculations utilized the Ahlrichs' triple-zeta valence basis set augmented by one set of polarization functions (TZVP); for tellurium, the corresponding ECP basis set was used. All calculations were done with the Gaussian 03 program package.


The sum of the covalent radii is 2.34 Å for Se-Se and 2.74 Å for Te-Te.


Te-Te bond lengths of ditellurides are typically in the range 2.68-2.71 Å, but a value of 2.77 Å has been reported recently for the highly crowded system (PhMe3Si)2Te2C(SiMe3)2Ph; T. M. Klaptocz, B. Krumm, H. Nöth, J. C. Gálvez-Ruiz, K. Polborn, I. Schwab, and M. Suter, Inorg. Chem., 2005, 44, 5254.


The Se–I contact of 3.150(1) Å exceeds the upper limit of 3.00 Å proposed by Du Mont et al. to distinguish between ‘three-center-four electron bonds’ and ‘secondary bonds’.