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Year: 2006

Version:

Please cite the original version:

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

Jari Konu, Tristram Chivers* and Heikki M. Tuononen

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

The coordination chemistry of the dichalcogenimidodiphosphinate ligands [N(PR_2E)_2]^+. 1 (E = O, S, Se) has been studied extensively. 1 This pervasive interest arises from a number of potential uses e.g., 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 anion metal complexes of the isopropl derivatives 1a and 1b are sufficiently volatile to serve as single-source precursors for the production of thin semi-conducting films. 5 The cadmium complex of 1b produces CdSe quantum dots in a solvothermal reaction. 6

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\begin{align*}
1a (E = S) & \quad 1b (E = Se) \\
1c (E = Te) & \\
2a (E = S) & \quad 2b (E = Se) \\
2c (E = Te)
\end{align*}
\]

The neutral precursors to the anionic ligands 1a and 1b are readily made by direct reaction between HN(PR_2E) and elemental sulfur or selenium, respectively. 7 But this reaction is not successful for the synthesis of HN(PR_2Te). Consequently, we have developed a different approach to the synthesis of the anionic tellurium ligands [N(PR_2Te)_2]^: (R = Pr, Ph) that involves metatllation of HN(PR_2) with NaH prior to reaction with tellurium. 8, 9 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. 8, 9 The ditelluride 2c may be considered to be the dimer of the tellurium-centered radical [TePPrN(PPrP)Te][]. 9, 10 The discovery of 2b and 2c 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 dichalcogenimidodiphosphinate ligand system. In this communication we describe the synthesis, molecular and electronic structures of the salts [N(PPrSe)_2]I (4) and [N(PPrTe)_2]I (5), which contain the cyclic cations 3b and 3c, respectively. These formally 6e-electron cations represent a novel class of inorganic ring system 11 and provide a new feature of the chemistry of dichalcogenimidodiphosphinates.

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 [(tmdea)NaN(P\text{Pr}_2\text{E})] (E = Se, Te) with one equivalent of I2 at -78 °C produce the iodide salts 4 and 5 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{Pr}_{2}P\text{-units for both compounds. In the}^1H 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. Consistently, the \textsuperscript{13}C\textsuperscript{[1H]} NMR spectra show two singlets for the Me-groups and a multiplet for the \textalpha-carbons of the \text‘Pr’-groups arising from an AX\textalpha’ spin system. 14 The \textsuperscript{31}P\textsuperscript{[1H]} NMR spectra of 4 and 5 exhibit broad singlets at 92.9 and 68.0 ppm, respectively, with broad halogen satellites (\textupsilon_{J_{Se,P}} \approx 395 Hz, \textupsilon_{J_{Te,P}} \approx 1035 Hz). These broad signals do not resolve into the expected two resonances (mutually coupled doublets) even at -60 °C indicating conformational non-rigidity within the rings persists at low temperature. The \textsuperscript{77}Se NMR spectrum of 4 exhibits a broad doublet at 297 ppm (\textupsilon_{J_{Se,P}} \approx 420 Hz), but the \textsuperscript{125}Te NMR resonance for 5 could not be observed owing to the low solubility of the compound.

X-ray crystallographic analyses revealed that 4 and 5 are comprised of five-membered [NP\text{E}_2]^+ cations and an iodide counter-ion that interacts with one of the chalcogen atoms of the cation resulting in inequivalent \text‘Pr’-units. The molecular structure (Figure 1) and crystal packing (Figure 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 E···I interactions show only a slight variation in 5 (3.430(1) Å and 3.495(1) Å), whereas the corresponding difference is more pronounced in 4 (3.150(1) and 4.006(1) Å). The Te···I contacts in 5 are comparable to theionic interactions found in EtTe\textsuperscript{+...}$\textsuperscript{-} (3.418 Å) 15 and in [((BuNH)Te\textsuperscript{+}(µ-NBu)\textsuperscript{-}Te(µ-O)]\textsuperscript{-} (3.410(1) Å) and 3.445(1) Å). 16 The shorter Se···I interaction in 4 is somewhat longer than that observed in Ph\textsubscript{2}Se\textsubscript{2}I (2.992 Å), 17 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). 18

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In contrast to the planarity of related chalcogen-nitrogen cations [(RCN)E]⁺ (E = S, Se),[106] [E₂(N)]⁺ (E = S, Se),[20] and the nitrogen-rich system [S₂N]+,[21] 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.[22] 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 2e).[9] 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.[26]

For comparison, the Se-Se bond lengths in the six π-electron, five-membered cyclic cations in the salts [PhCNSe₂][PF₆]₂[27] and [Se₂N₂][AsF₆]₂[28] are 2.260(5) and 2.253(3) Å, respectively. The treatment of the lone pair on the extended structure. 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. The π-bond order is low, however, since the bonding effect of the E-E π-bonding orbital (HOMO-2) is essentially cancelled by the double occupation of the E-E π*-antibonding orbital (HOMO) and the third occupied π-orbital is primarily non-bonding nitrogen-centred 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 counter-ion into the σ* orbital (LUMO), cf. the formation of the triiodide I⁺ anion from an I⁻ ion and an I-I molecule.[30] DFT calculations confirm this view of the 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.

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 dichalcogenimidodiphosphinanes. Electrochemical studies of these systems and the synthesis of ion-separated salts are in progress.

Notes and references

Crystal data for 4: C₃H₇H₃-N₃P·Se₂, Mᵡ = 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, ρadj = 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 (Rᵡ = 0.0377), R₁ = 0.0348 [for 3035 reflections with I > 2σ(I)] and wR₁ = 0.0861 (for all data). Crystal data for 5: C₃H₇H₃-N₃P·Te₂, Mᵡ = 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, ρadj = 2.174 g cm⁻³, µ = 4.786 mm⁻¹, T = 173(2) K, 5647 reflections collected (θ range = 2.72-25.02°), 3201 unique (Rᵡ = 0.0391), R₁ = 0.0317 [for 2994 reflections

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: Se2-P2·2229(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 2.436(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-Se2 2.839(1) [2.884], Te1···I1 3.430 (1), P1-N1-P2 133.2(4) [129.5], N-P-Te 109.5 [111.2], τ P1-Se1-Se2-P2-25.05(7) [-27.2].

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 3.495(1) Å, Te1···I1 3.430 (1), P1-N1-P2 133.2(4) [129.5].

Figure 3. Frontier orbitals in the [N(PPr₃)E⁺] (E = Se, Te) rings. Te-Te bond length in the cation ([Te₂Se₂)Cl]⁺, in which one of the Te atoms is three-coordinate, is 2.731(2) Å.[28,29] DFT calculations have provided important insights into the electronic structures in the cyclic cations 3b and 3c.[22] 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.


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


18  Mulliken population analysis shows that a significant portion of the positive charge is localized on the phosphorus atoms: P 0.23, N 0.22, Se 0.01 in 3b and P 0.30, 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 package program.


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


25  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 PhMe₂C≡Te·Te·Me₂CSiPh: T. M. Klapötke, B. Krumm, H. Nöth, J. C. Gámez-Ruiz, K. Polborn, I. Schwab, and M. Suter, Inorg. Chem., 2005, 44, 5254.

26  The structures of the almost linear anion [Te₂Ph₂] (Te-Te 2.939(1) and 3.112(1) Å) and the bent cation [Te₅Ph₂] (Te-Te 2.979(1) and 3.049(1) Å) have been compared to that of I: A. C. Hillier, S.-Y. Liu, A. Sella and M. R. I. Elsegoud, Angew. Chem. Int. Ed. Engl., 1999, 38, 2745; J. Jeske, W. du Mont and P. G. Jones, Angew. Chem. Int. Ed. Engl., 1997, 36, 2219.

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