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The Cyclic $[N(P^iPr_2E)_2]^+$ ($E = Se, Te$) Cations: A New Class of Inorganic Ring System

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The two-electron oxidation of $[(tmeda)NaN(P^iPr_2E)_2]$ with iodine produces the cyclic $[N(P^iPr_2E)_2]^+$ ($E = Se, Te$) cations, which exhibit long E-E bonds in the iodide salts

The coordination chemistry of the dichalcogenoimidodiphosphinate 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 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.⁵ The cadmium complex of **1b** produces CdSe quantum dots in a solvothermal reaction.⁶

The neutral precursors to the anionic ligands **1a** and **1b** are readily made by direct reaction between $HN(P^iPr_2)_2$ and elemental sulfur or selenium, respectively,⁷ but this reaction is not successful for the synthesis of $HN(P^iPr_2Te)_2$. Consequently, we have developed a different approach to the synthesis of the anionic tellurium ligands $[N(PR_2Te)_2]^-$ ($R = ^iPr, Ph$) that involves metallation of $HN(PR_2)_2$ 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 $[TeP^iPr_2N^iPr_2P^iPr_2Te]^\cdot$.^{9, 10} The discovery of **2b**¹⁰ and **2c**⁹ 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 $[N(P^iPr_2Se)_2]I$ (**4**) and $[N(P^iPr_2Te)_2]I$ (**5**), which contain the cyclic cations **3b** and **3c**, respectively. These formally 6π -electron cations represent a novel class of inorganic ring system¹¹ 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 $[(tmeda)NaN(P^iPr_2E)_2]$ ($E = Se, Te$) with one equivalent of I_2 at $-78^\circ C$ produce the iodide salts **4** and **5** in 90 and 92 % yields, respectively.[‡] The surprisingly air-stable compounds¹³ were characterized by multinuclear NMR spectroscopy and by X-ray crystallography.[§] The NMR spectra reveal inequivalent iPr_2P -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 $^{13}C\{^1H\}$ NMR spectra show two singlets for the Me-groups and a multiplet for the α -carbons of the iPr -groups arising from an AXX' spin system.¹⁴ The $^{31}P\{^1H\}$ NMR spectra of **4** and **5** exhibit broad singlets at 92.9 and 68.0 ppm, respectively, with broad chalcogen satellites ($^1J_{Se,P} \approx 395$ Hz, $^1J_{Te,P} \approx 1035$ Hz). These broad signals do not resolve into the expected two resonances (mutually coupled doublets) even at $-60^\circ C$ indicating conformational non-rigidity within the rings persists at low temperature. The ^{77}Se NMR spectrum of **4** exhibits a broad doublet at 297 ppm ($^1J_{Se,P} \approx 420$ Hz), but the ^{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 $[NP_2E_2]^+$ cations and an iodide counter-ion that interacts with one of the chalcogen atoms of the cation resulting in inequivalent iPr_2P -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 $E \cdots I$ interactions show only a slight variation in **5** (3.430(1) and 3.495(1) Å), whereas the corresponding difference is more pronounced in **4** (3.150(1) and 4.006(1) Å). The $Te \cdots I$ contacts in **5** are comparable to the ionic interactions found in $Et_3Te^+ \cdots I^-$ (3.418 Å)¹⁵ and in $\{[(tBuNH)Te^+(\mu-N^iBu)_2Te(\mu-O)]_2\} \cdots (I)_2$ (3.410(1) and 3.445(1) Å).¹⁶ The shorter $Se \cdots I$ interaction in **4** is somewhat longer than that observed in $Ph_2Se_2I_2$ (2.992 Å),¹⁷ which also contains a $Se-Se \cdots I$ -unit. The second $Se \cdots I$ 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**: Se2-P2 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 2.436(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-Te2 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-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^a 4.006(1) Å and Te2...I1^a 3.495(1) Å, ^a x, y+1.

In contrast to the planarity of related chalcogen-nitrogen cations ⁹⁵ [RCN₂E₂]⁺ (E = S, Se),¹⁹ [E₃N₂]²⁺ (E = S, Se),²⁰ and the nitrogen-rich system [S₂N₃]⁺,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-iodine interactions cause a significant perturbation of the P-E bonds ¹⁰⁵ (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**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.²⁶ ¹¹⁰ For comparison, the Se-Se bond lengths in the six π -electron, five-membered cyclic cations in the salts [PhCN₂Se₂][PF₆]²⁷ and [Se₃N₂][AsF₆]₂²⁰ are 2.260(5) and 2.253(3) Å, respectively. The

Figure 3. Frontier orbitals in the [N(P'PrE)₂]⁺ (E = Se, Te) rings.

Te-Te bond length in the cation [(Te₂SN₂)Cl]⁺, in which one of the Te atoms is three-coordinate, is 2.731(2) Å.^{28, 29}

¹¹⁵ 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 ¹²⁰ 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. ¹²⁵ 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 I₃⁻ anion from an I⁻ ion and an I-I molecule.^{30, 31} DFT calculations confirm this view of the of the E...I ¹³⁰ 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. ¹³⁵

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 ¹⁴⁰ sequence -1/0/+1 for dichalcogenoimidodiphosphinates. Electrochemical studies of these systems and the synthesis of ion-separated salts are in progress.

Notes and references

- ¹⁴⁵ Crystal data for **4**: C₁₂H₂₈I₁N₁P₂Se₂, *M_r* = 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, ρ_{calcd} = 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 (*R*_{int} = 0.0377), *R*₁ = 0.0348 [for 3035 reflections with *I* > 2 σ (*I*)] and *wR*₂ = 0.0861 (for all data). Crystal data for **5**: C₁₂H₂₈I₁N₁P₂Te₂, *M_r* = 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, ρ_{calcd} = 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 (*R*_{int} = 0.0391), *R*₁ = 0.0317 [for 2994 reflections

with $I > 2\sigma(I)$ and $wR_2 = 0.0817$ (for all data). 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 SHELXS-97 and the model refined by using SHELXL-97.³²

‡ The reagent $[N(P'Pr_2Te)_2]_2$ was prepared by the method described earlier⁹ and $[(tmeda)NaN(P'Pr_2E)_2]$ (E = Se, Te) were prepared by modifications of the procedure reported for $[(tmeda)NaN(PPh_2Te)_2]$.⁸

4: A solution of $[(tmeda)NaN(P'Pr_2Se)_2]$ (0.273 g, 0.50 mmol) in toluene (30 mL) was cooled to -78 °C and a cold (0 °C) solution of I_2 (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 $C_{12}H_{28}I_2N_2P_2Se_2$: C 27.03, H 5.29, N 2.63; found: C 27.10, H 5.24, N 2.85. ¹H NMR (D_8 -THF, 23 °C): δ = 2.73 [2 x sept., ³J(H,H) = 7 Hz, 4H; CH(CH₃)₂], 1.37 [dd, ³J(H,H) = 7 Hz, ³J(H,P) = 18 Hz, 12H; CH(CH₃)₂], 1.35 [dd, ³J(H,H) = 7 Hz, ³J(H,P) = 20 Hz, 12H; CH(CH₃)₂]; ¹³C{¹H} NMR: δ = 33.2 (m, 4C; CH(CH₃)₂), 18.6 (s, 4C; CH(CH₃)₂), 17.7 (s, 4C; CH(CH₃)₂); ³¹P{¹H} NMR: δ = 92.9 (br, ¹J(⁷⁷Se,P) $\approx$ 395 Hz); ⁷⁷Se NMR: δ = 297 (br, d, ¹J(⁷⁷Se,P) $\approx$ 420 Hz). Yellow, block-like crystals of **4** were grown from a THF:toluene solution.

5 from [(tmeda)NaN(P'Pr₂Te)₂]: The salt **5** was obtained as a dark red, crystalline powder (0.291 g, 92%) from the reaction of $[(tmeda)NaN(P'Pr_2Te)_2]$ (0.321 g, 0.50 mmol) in toluene (30 mL) with I_2 (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 $C_{12}H_{28}I_2N_2P_2Te_2$: C 22.86, H 4.48, N 2.22; found: C 22.68, H 4.39, N 2.33. ¹H NMR (D_8 -THF, 23 °C): δ = 2.62 [2 x sept., ³J(H,H) = 7 Hz, 4H; CH(CH₃)₂], 1.35 [dd, ³J(H,H) = 7 Hz, ³J(H,P) = 18 Hz, 12H; CH(CH₃)₂], 1.31 [dd, ³J(H,H) = 7 Hz, ³J(H,P) = 20 Hz, 12H; CH(CH₃)₂]; ¹³C{¹H} NMR: δ = 33.1 (m, 4C; CH(CH₃)₂), 19.6 (s, 4C; CH(CH₃)₂), 18.1 (br, s, 4C; CH(CH₃)₂); ³¹P{¹H} NMR: δ = 68.0 (br, ¹J(¹²⁵Te,P) $\approx$ 1035 Hz). Dark red, block-like crystals of **5** were grown from a THF:toluene solution.

5 from 2c: $[N(P'Pr_2Te)_2]_2$ (0.100 g, 0.10 mmol) and I_2 (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 -78 °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%).

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