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COMMUNICATION

Planar P_6E_6 ($E = \text{Se}, \text{S}$) macrocycles incorporating P_2N_2 scaffolds†‡Andreas Nordheider,^{ab} Tristram Chivers,^{*a} Ramalingam Thirumoorthi,^a Ignacio Vargas-Baca^c and J. Derek Woollins^b

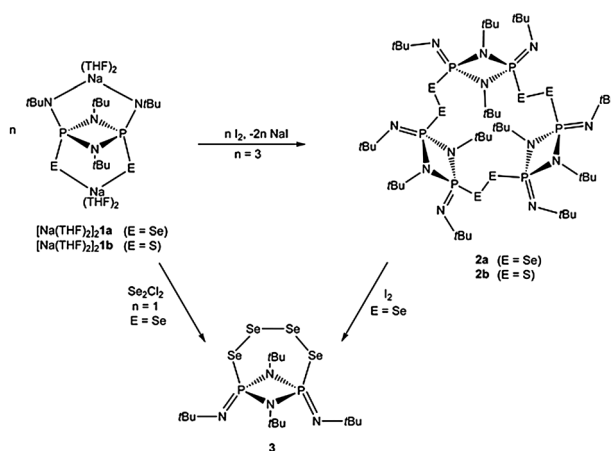
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Oxidation of alkali metal derivatives of the dianions $[E(\text{tBuN})P(\mu\text{-N}'\text{tBu})_2P(\text{N}'\text{tBu})E]^{2-}$ ($E = \text{S}, \text{Se}$) with I_2 produces 15-membered macrocycles in which a planar P_6E_6 motif is stabilised by perpendicular P_2N_2 scaffolds.

Current interest in inorganic macrocycles stems from their potential applications as multidentate ligands and in metal-templated ring transformations.¹ For example, silver ions have been shown to promote the ring expansion of cyclosiloxanes.² Ring systems that incorporate $P^{\text{III}}_2N_2$ building blocks bridged by imido (NH) linkages have been shown to incorporate halide ions by Wright and co-workers.^{3,4} An extension of their work to monoselenido ($-\text{Se}-$) linkages produced the intriguing hexameric $P^{\text{V}}-P^{\text{III}}$ macrocycle $[\text{Se}=\text{P}(\mu\text{-N}'\text{tBu})_2\text{P}(\mu\text{-Se})]_6$ via a reductive coupling procedure using Na metal in boiling toluene.⁵

In extensive studies of the redox behavior of acyclic monoanions of the type $[\text{EPR}_2\text{NPR}_2\text{E}]^-$ ($E = E' = \text{S}, \text{Se}, \text{Te}$; $E = \text{Te}, E' = \text{S}, \text{Se}$; $R = \text{'Pr}, \text{'Bu}$) we have shown that one-electron oxidation with I_2 results in chalcogen–chalcogen bond formation to give unusual dichalcogenides, which may adopt either acyclic or spirocyclic structures.^{6–8} The facility with which this transformation occurs suggested that the oxidation of the dianions $[E(\text{tBuN})P(\mu\text{-N}'\text{tBu})_2P(\text{N}'\text{tBu})E]^{2-}$ (**1a**, $E = \text{Se}$; **1b**, $E = \text{S}$)⁹ might afford $P^{\text{V}}-P^{\text{V}}$ macrocycles in which dichalcogenido linkages $-\text{E}-\text{E}-$ are bridged by P_2N_2 scaffolds. In this communication we disclose that this methodology produces the novel inorganic macrocycles $[\text{'BuN}=\text{P}(\mu\text{-N}'\text{tBu})_2\text{P}(=\text{N}'\text{tBu})(\mu\text{-E}-\text{E})]_3$ (**2a**, $E = \text{Se}$; **2b**, $E = \text{S}$) (Scheme 1), which have been characterised in solution and the solid state by multinuclear NMR spectra and X-ray crystallography supported by DFT calculations. Surprisingly, the P_6E_6 motifs in **2a** and **2b** adopt a planar arrangement in the solid state. In addition, an interesting ring transformation to give the monomeric tetraselenide

Scheme 1 Synthesis of **2a**, **2b** and **3**.

$[\text{'BuN}=\text{P}(\mu\text{-N}'\text{tBu})_2\text{P}(=\text{N}'\text{tBu})(\mu\text{-Se}-\text{Se}-\text{Se}-\text{Se})]_3$ (**3**) occurs when the trimeric diselenide **2a** is oxidised with I_2 .

The oxidation of the sodium or potassium salts of **1a** or **1b** with one equivalent of I_2 in THF or toluene produces a mixture of phosphorus-containing products from which **2a** or **2b** can be isolated as orange or yellow crystals in 35% and 22% yields, respectively, when the sodium salt is used as the precursor. The by-products of this reaction are the diprotonated derivatives $[(\text{'BuNH})E=\text{P}(\mu\text{-N}'\text{tBu})_2\text{P}=\text{E}(\text{NH}'\text{tBu})] [\text{H}_2\text{1a}$ ($E = \text{Se}$) and $\text{H}_2\text{1b}$ ($E = \text{S}$)]⁹ and a third P,Se-containing compound that was subsequently identified as the tetraselenide $[\text{'BuN}=\text{P}(\mu\text{-N}'\text{tBu})_2\text{P}(=\text{N}'\text{tBu})(\mu\text{-Se}-\text{Se}-\text{Se}-\text{Se})]$ (**3**) on the basis of ^{31}P and ^{77}Se NMR spectra (*vide infra*). Compound **2a** is air-stable solid whereas **2b** is air-sensitive and forms $\text{H}_2\text{1b}$ on exposure to moisture. Both compounds exhibit very limited solubility in solvents such as THF, toluene, and dichloromethane and form the diprotonated derivatives $\text{H}_2\text{1a}$ and $\text{H}_2\text{1b}$ upon prolonged contact with solvents.

The ^{31}P NMR spectrum of **2a** in toluene exhibits a singlet at -67.3 ppm flanked by two sets of ^{77}Se satellites. Assuming the formation of a $\text{P}-\text{Se}-\text{Se}-\text{P}$ grouping, the coupling constants were determined to be $^1J(\text{P},\text{Se}) = 428$ Hz and $^2J(\text{P},\text{P}) = 19.5$ Hz based on simulation as an $\text{AA}'\text{X}$ system (where X represents ^{77}Se and A, A' are the magnetically inequivalent phosphorus atoms in the isotopomer that gives rise to the satellite resonances).¹⁰ The ^{77}Se NMR spectrum is comprised of a doublet centered at 408.6 ppm with $^1J(\text{P},\text{Se}) = 429$ Hz (based on simulation as an AXX' system where A represents ^{77}Se and X, X' are the

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‡ Electronic supplementary information (ESI) available: Experimental and crystallographic data in pdf format. CCDC 867162 (**2a**), 876357 (**2b**) and 867163 (**3**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2cc32809g

magnetically inequivalent phosphorus atoms in the most abundant isotopomer with spin-active Se nuclei; $^2J(\text{P},\text{Se})$ was obscured by the intense central resonance). Thus, the solution NMR spectra of **2a** are consistent with the formation of a P–Se–Se–P linkage with chemically equivalent, but magnetically inequivalent, phosphorus environments. Similarly, the ^{31}P NMR spectrum of **2b** shows a singlet at -48.7 ppm consistent with chemically equivalent phosphorus centres. Interestingly, however, the solid-state ^{31}P NMR CP-MAS spectrum of **2a** consists of two resonances at -67.6 and -59.8 ppm suggesting the presence of two phosphorus environments in the crystal (Fig. S1, ESI†). Consistently, the solid-state ^{31}P NMR CP-MAS spectrum of **2b** also exhibits two resonances at -61.0 and -34.2 ppm. The presence of the Se–Se functionality in **2a** is supported by a very strong Raman band at 294 cm^{-1} , cf. 282 cm^{-1} in octaselenocyclododecane $(-\text{CH}_2-\text{Se}-\text{Se}-)_4$.¹¹

The mass spectrometric data for **2a** and **2b** are indicative of trimeric structures. A MALDI-TOF mass spectrum of **2a** exhibits a group of peaks centered at $m/z = 1583$ $[\text{M} + 3\text{Na}]^+$ with the appropriate relative intensities for six selenium atoms, while the EIMS of **2b** shows a parent ion at $m/z = 1231$ $(\text{M} + \text{H})^+$. Single crystals of **2a** suitable for an X-ray structural analysis were obtained by recrystallization from a toluene–hexane mixture. The molecule crystallizes in the hexagonal space group $P6_3/m$ with two molecules in the unit cell. As illustrated in Fig. 1a, the macrocycle **2a** is comprised of a 15-membered $\text{P}_6\text{N}_3\text{Se}_6$ ring in which three P_2N_2 rings are bridged by three diselenido ($-\text{Se}-\text{Se}-$) units. Intriguingly, the P_6Se_6 framework is essentially planar with P–Se–Se–P torsion angles of 180° and the P_2N_2 rings are situated perpendicular to this plane (Fig. 1b). For comparison, the only macrocycles containing the P–Se–Se–P unit reported to date have torsion angles in the range 93.0 – 107.5° ¹² and the C–Se–Se–C torsion angles in $(-\text{CH}_2-\text{Se}-\text{Se}-)_4$ are 93.0° and 98.2° .¹¹ Single crystals of **2b** were obtained by recrystallisation from hexane and found to be isomorphous with **2a**. The heterocycle **2b** also has a trimeric structure with structural features that are similar to those of **2a**, i.e. a planar P_6S_6 motif with P–S–S–P torsion angles of 180° (see Fig. S2 and S3, ESI† for details). The Se–Se bond lengths in **2a** are similar to those found in the aforementioned cyclic diselenides,¹² whereas the S–S bond lengths of $2.121(2)\text{ \AA}$ in **2b** are significantly longer (by ca. 0.05 \AA) than the corresponding values in cyclic compounds containing a $\text{P}^{\text{V}}-\text{S}-\text{S}-\text{P}^{\text{V}}$ unit.¹³ The planar conformations of **2a** and **2b** in the solid state impose close contacts between three of the chalcogen atoms ($d(\text{Se1}-\text{Se1}') = 3.315\text{ \AA}$ for **2a**, $d(\text{S1}-\text{S1}') = 3.311\text{ \AA}$ for **2b**, cf. sum of van der Waals radii for two chalcogen atoms = 3.80 and 3.60 \AA for Se and S, respectively).¹⁴

The structural and NMR data for **2a** and **2b** raise several questions that have been addressed through DFT calculations on the Se system. Firstly, why is a single resonance observed in the solution ^{31}P NMR spectra whereas two resonances are apparent in the solid-state ^{31}P NMR spectra consistent with the X-ray crystal structures? Is the structure flexible enough to allow a dynamic exchange process? Initial attempts to optimize a flat structure for a model of **2a** in which $t\text{Bu}$ groups were replaced by Me groups employing GGA DFT (PW91) and B3LYP (which includes HF correlation)^{15,16} led to puckered structures even when the crystallographic coordinates were used as starting point. However, the use of the new dispersion-corrected potential

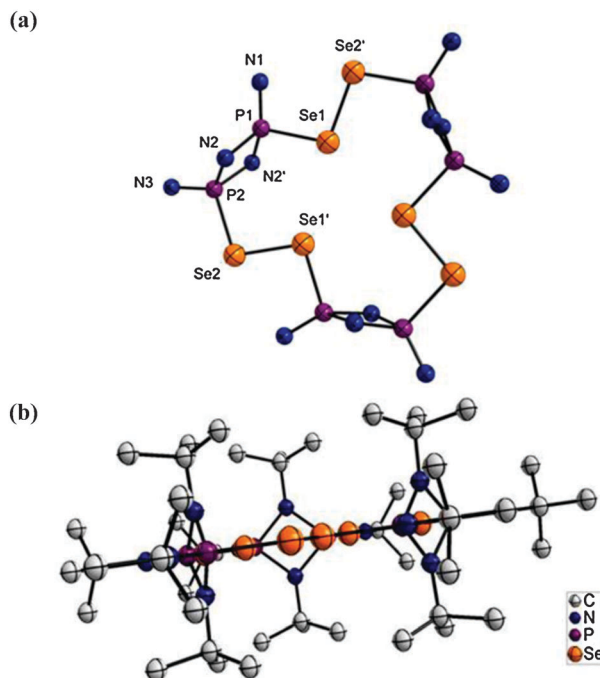


Fig. 1 Molecular structure of **2a**. Hydrogen atoms have been omitted for clarity. (a) View from on top showing the atomic numbering scheme. Selected bond distances (\AA) and angles ($^\circ$) [calculated values are given in brackets]: Se1–Se2' 2.3217(14), [2.384] P1–Se1 2.253(2) [2.257], P2–Se2 2.262(2) [2.277], N1–P1 1.507(9) [1.533], N2–P1 1.695(5) [1.699], N2–P2 1.695(6) [1.692], N3–P2 1.501(7) [1.529]; P1–N2–P2 96.0(3) [97.4], N2–P1–N2 83.8(4) [82.1], N2'–P2–N2 83.7(4) [82.5], P1–Se1–Se2' 97.79(7) [100.0], P2–Se2–Se1' 98.63(7) [98.43]. (b) Side-on view showing the planarity of the P_6Se_6 framework with the P_2N_2 rings perpendicular to this plane.

B3LYP-D3¹⁷ available in ADF succeeded in optimizing a flat structure with bond parameters that were in very good agreement with the experimental values. The puckered structure was refined with the same method; in the resulting geometry the selenium atoms are positioned up to 1.0 \AA from the average plane defined by the phosphorus atoms (Fig. 2). This puckered structure was found to be 30.5 kJ mol^{-1} below the flat conformation, without zero-point energy correction. In solution, therefore, it is likely that the ring is puckered and will undergo fast conformational fluxionality leading to an averaged resonance in the ^{31}P NMR spectrum. Unfortunately, the low solubility of **2a** thwarted attempts to obtain low-temperature solution NMR spectra.

Secondly, does the close approach of three of the chalcogen atoms in the solid state enable an intramolecular $\text{E} \cdots \text{E}$ bonding interaction $[\text{lp}(\text{E}) \rightarrow \sigma^*(\text{E}-\text{E})]$ that stabilises the flat structure? According to the calculated Nalewajski–Mrozek¹⁸ bond orders



Fig. 2 Space filling model of the optimized puckered structure for **2a**.

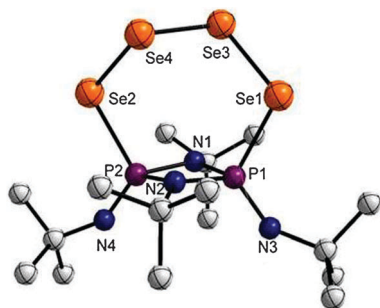


Fig. 3 Molecular structure of **3**. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Se1–Se3 2.3371(19), Se2–Se4 2.3317(19), Se3–Se4 2.321(2), P1–Se1 2.280(3), P2–Se2, 2.275(3), P1–N3 1.503(10), P2–N4 1.494(10), P–N(bridging) range 1.685(9)–1.698(9); Se4–Se3–Se1 103.20(7), Se3–Se4–Se2 103.41(7).

for **2a**, there is no significant Se...Se bonding interaction. Considering the small difference in energy between the two optimized structures, we suggest that the geometry observed in the solid state is a consequence of a lattice effect. Packing is more efficient with flat molecules.

We also investigated the reaction of the dianion **1a** with Se₂Cl₂ in a 1:1 molar ratio in toluene as a possible source of polyselenides stabilised by P₂N₂ scaffolds. This reaction produced an orange solid, which was identified as the tetraselenide [tBuN=P(μ-N^tBu)₂P(=N^tBu)(μ-Se–Se–Se–Se)]₃ (**3**) (56% yield) (Scheme 1). Crystals of **3** suitable for an X-ray structural determination were obtained by recrystallization from *n*-hexane. As illustrated in Fig. 3, compound **3** is a puckerd seven-membered ring comprised of a P₂N₂ scaffold bridged by a tetraselenido (–Se–Se–Se–Se–) unit. The Se–Se bond lengths in **3** are similar to those in **2a** and the P–Se distances are typical for P^V–Se single bonds.^{5,12} The Se1–Se3–Se4–Se2 torsion angle is 94.44(8)°. A very strong Raman band at 274 cm^{–1} can be attributed to a Se–Se stretching vibration.

The ⁷⁷Se NMR spectrum of **3** in d₈-THF at 25 °C consists of two resonances consistent with the presence of two pairs of equivalent Se atoms in solution. A low-field pseudo-triplet at 673.0 ppm [²*J*(Se,P) = 20 Hz, ²*J*(P,P) = 13 Hz] is attributed to the Se3,Se4 pair, while the pseudo-doublet of doublets centered at 336.7 ppm (¹*J*(Se,P) = 524 Hz, ³*J*(Se,P) = 6 Hz) is assigned to Se1,Se2. The ³¹P{¹H} NMR spectrum of **3** in d₈-THF shows a resonance at –50.8 ppm with ⁷⁷Se satellites (¹*J*(P,Se) = 524 Hz).

The very close similarity between the ³¹P NMR parameters for **3** and those of the by-product from the I₂ oxidation of the dianion **1a**, especially the characteristic one-bond ³¹P–⁷⁷Se coupling of ca. 525 Hz (*cf.* 429 Hz for **2a**), strongly suggest that the by-product formed in the synthesis of **2a** (*vide supra*) is the tetraselenide **3**. In order to explain the formation of **3** in that oxidative transformation, we treated the trimeric diselenide **2a** with an equimolar amount of I₂ in toluene (or THF) and, on the basis of multinuclear (¹H, ¹³C, ³¹P and ⁷⁷Se) NMR spectra, observed that the tetraselenide **3** is

indeed formed upon oxidation of **2a**. Thus, the P₂N₂-supported diselenido ligand in **2a** is converted to the tetraselenido ligand in **3** *via* two-electron oxidation by I₂.

In summary, we have demonstrated the versatility of the oxidative approach to chalcogen-containing macrocycles incorporating P₂N₂ scaffolds by the synthesis of sulfur and selenium systems containing –E–E– functionalities. In contrast to the reductive coupling approach,⁵ mild oxidation can potentially be extended to related, but more labile, P–Te systems.¹⁹ These new macrocycles embody a planar P₆E₆ motif in the solid state, which is attributed to packing effects. However, a puckerd structure is energetically favourable in solution.

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