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Catenated and Spirocyclic Polychalcogenides from Potassium Carbonate and Elemental Chalcogens †

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The reaction of potassium carbonate with elemental sulfur or selenium in acetone in the presence of [PPN]Cl produces *catena*-$[S_{12}]^{2-}$, the longest structurally characterised polysulfide dianion, or *spiro*-$[Se_{11}]^{2-}$ as ion-separated $[PPN]^+$ salts.

Introduction

The critical role played by polysulfide dianions $[S_n]^{2-}$ and related radical monoanions $[S_n]^{\bullet-}$ across the chemical, physical and biological sciences,[1] notably in the development of lithium-sulfur batteries,[2] in biological signaling involving NO,[3] in geochemical processes including metal transport,[4] and as reagents for the synthesis of organosulfur compounds,[1,5] has re-generated interest in the fundamental chemistry of these simple homoatomic species. Although small, acyclic radical monoanions $[S_n]^{\bullet-}$ (n = 2,3,4) are known to be stabilised in zeolitic matrices,[1,6] the only single-crystal structural characterisation of these paramagnetic species is the hexasulfide (n = 6) in $[PPh_4]S_6$, which has a cyclic structure with *two* long S–S bonds (263.3 pm) connecting two S_3 units.[7] However, DFT calculations yield a global minimum structure of C_2 symmetry with only *one* long S–S bond (294.3 pm).[8]

In the context of sulfur ↔ sulfide redox chemistry the frequently cited eqn. (1)[2c,d,g] depicts the mass balance, but it does not explain how *cyclo*-S_8 is formed.

$$[S_8]^{2-} \longrightarrow [S_6]^{2-} + 1/4\ \textit{cyclo}\text{-}S_8 \qquad (1)$$

As suggested in recent reviews, longer chain polysulfides $[S_n]^{2-}$ (n > 8) should be considered for this process.[1,6] For years, the longest known dianionic polysulfide chain was the nonasulfide in $[K_2(THF)]_2S_9$.[9,10] Very recently, the isolation and structural characterization of the first decasulfide dianion salt, [(222-cryptand)K]$_2S_{10}$, was reported by Wang and co-workers.[11] An X-ray diffraction study confirmed the anticipated chain structure of the $[S_{10}]^{2-}$ dianion. Interestingly, the synthesis of a deep violet solid claimed to be "$[PPN]_2S_{12}$" (PPN = $(Ph_3P)_2N$) has been reported by Seel and co-workers, who have also shown that treatment of this polysulfide with NO or $[PPN]NO_2$ in acetone or DMF generates the biologically significant, red anion $[SSNO]^-$.[12] More recently, Pluth and co-workers demonstrated that this acyclic anion is formed by reaction of NO with a solution of the blue radical anion $[S_3]^{\bullet-}$, which was generated from *cyclo*-S_8 and $[NBu_4][SH]$ in THF.[3b] The reaction of *cyclo*-S_8 with [PPN]SH in ethanol had previously been shown to give orange-red $[PPN]S_7$ in high yield.[13] Significantly, both $[PPN]S_7$ and "$[PPN]_2S_{12}$" produce blue $[S_3]^{\bullet-}$ in acetone or acetonitrile solutions as manifested by a strong absorption at 620 nm in the visible spectrum.[12,13] Furthermore, the radical anion $[S_3]^{\bullet-}$ has been invoked as the reactive species in recent applications of a mixture of sulfur and an alkali-metal carbonate for the synthesis of a variety of organosulfur compounds.[1,5]

Seel's identification of "$[PPN]_2S_{12}$" was based solely on elemental (C,H,N,S) analyses. However, the analytical data also fit the monomeric alternative $[PPN]S_6$. In this context, we describe here the structural characterization of $[PPN]_2S_{12}$ (**1**), which is readily prepared from the reaction of sulfur with potassium carbonate in acetone in the presence of [PPN]Cl. We have also applied this simple synthetic protocol to the corresponding selenium system in order to provide a direct comparison with the outcome of the sulfur reaction. In earlier work the reaction of potassium carbonate with *red* selenium in acetone at 23 °C in the presence of [PPN]Cl produced red crystals of $[PPN][Se_5C(Se)COMe]$ as a minor product (26% yield); the major product of this reaction, a dark green solid, could not be identified in this earlier study.[14] Inspired by the structural characterization of **1**, we have now determined the solid-state structure of this product by X-ray crystallography and shown it to be $[PPN]_2Se_{11}$ (**2**).

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† Electronic Supplementary Information (ESI) available: Full experimental and characterization details for **1** and **2**. CCDC (**1**) and (**2**). For ESI and crystallographic data in CIF or other electronic format see DOI:

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Results and discussion

The dodecasulfide salt $[PPN]_2S_{12}$ was prepared by a slight modification of the original procedure published by Seel *et al.*[12] Treatment of a suspension of bis(triphenylphosphoranylidene)ammonium (= PPN) chloride and potassium carbonate in acetone with an excess of elemental sulfur led to a blue colouring, followed by formation of a deep orange-red solution. After standing at r.t. for 3 days, well-formed, dark red-violet crystals of $[PPN]_2S_{12}$ (**1**) had formed in the suspension. They were freed from unreacted starting materials by thoroughly washing with water and toluene and finally obtained in 12% isolated yield. After washing with CS_2 to remove the last traces of unreacted elemental sulfur the colour of the crystals changed to an intense red-brown (see ESI). A similar reaction of powdered elemental selenium with potassium carbonate in acetone led to a deep green solution, affording dark greenish-black crystals of $[PPN]_2Se_{11}$ (**2**) in 8% isolated yield. The outcome of the reaction was independent of the selenium reagent (red, black or grey), but the least reactive grey selenium required a prolonged reaction time at elevated temperature (several hours in refluxing acetone). For both **1** and **2**, the low isolated yields can be attributed to the retention of significant amounts of product in solution and the likely formation of other polychalcogenides.

Compounds **1** and **2** are moderately soluble in acetone and dissolve well in DMSO without decomposition under inert conditions. The dry solids are not very air-sensitive, but their solutions decompose rather quickly under atmospheric conditions. Both products were fully characterised by elemental analyses, IR, Raman, and NMR spectroscopy, thermal analyses (TG-DTA), and single-crystal X-ray diffraction. The elemental analyses are in good agreement with the proposed compositions, and the ^{1}H and ^{13}C NMR spectra in DMSO-d_6 confirmed the presence of the PPN^+ cation. Separated PPN^+ cations are present in the solid state as well, as the IR spectra of **1** and **2** are very similar to each other and to that of [PPN]Cl. In the Raman spectrum of **1**, characteristic vibrational bands of the $[S_{12}]^{2-}$ dianion were found at 383, 429(sh), 437, 508(sh), 516, and 534 cm^{-1}, which are in the same range as the bands previously observed for the related $[PPN]_2S_7$.[13] Meaningful ^{77}Se NMR data for **2** could not be obtained due to insufficient solubility.

Thermal analysis of **1** under an inert atmosphere of nitrogen revealed two decomposition processes between 188 °C and ca. 390 °C. The observed mass loss corresponds to elimination of two sulfur atoms, presumably to produce $[PPN]_2S_{10}$, followed by loss of eight sulfur atoms to give $[PPN]_2S_2$ (mass loss found: approx. 22%, calcd. for 10 S: 22.0%). The selenium compound **2** is thermally more stable than **1** and melts without decomposition at 156 °C. Simultaneous decomposition of the anion and the cation occurred in the temperature range 369–435 °C (see ESI for full details).

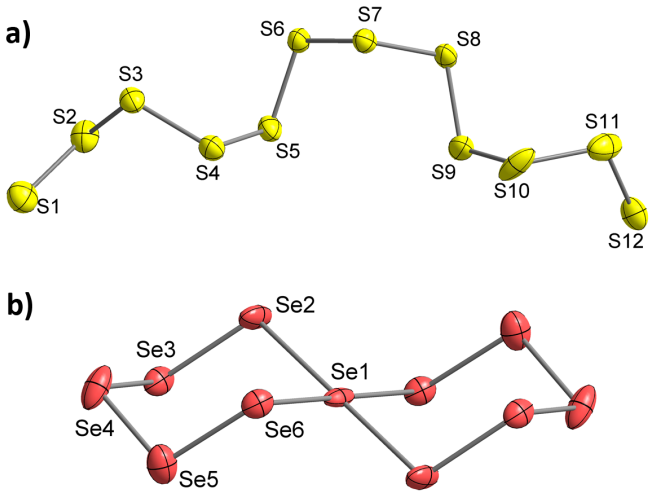

Figure 1. Molecular structures of *catena*-$[S_{12}]^{2-}$ (a) and *spiro*-$[Se_{11}]^{2-}$ (b) in the crystals of their respective PPN^+ salts. Displacement ellipsoids drawn at the 50% probability level. Selected bond lengths (pm) and bond angles (°) for **1**: S(1)-S(2) 201.3(2), S(2)-S(3) 204.7(2), S(3)-S(4) 207.1(2), S(4)-S(5) 205.5(2), S(5)-S(6) 205.0(2), S(6)-S(7) 204.3(2), S(7)-S(8) 205.3(2), S(8)-S(9) 204.4(2), S(9)-S(10) 207.6(3), S(10)-S(11) 203.4(3), S(11)-S(12) 199.6(3); S(1)-S(2)-S(3) 110.8(1), S(2)-S(3)-S(4) 111.23(9), S(3)-S(4)-S(5) 106.93(9), S(4)-S(5)-S(6) 107.37(8), S(5)-S(6)-S(7) 107.37(8), S(6)-S(7)-S(8) 106.11(8), S(7)-S(8)-S(9) 106.73(8), S(8)-S(9)-S(10) 106.8(1), S(9)-S(10)-S(11) 108.1(1), S(10)-S(11)-S(12) 109.7(1). Selected bond lengths (pm) and bond angles (°) for **2**: Se(1)-Se(2) 264.70(4), Se(1)-Se(6) 266.02(4), Se(2)-Se(3) 230.70(7), Se(3)-Se(4) 234.58(7), Se(4)-Se(5) 234.11(7), Se(5)-Se(6) 231.28(7); Se(2)-Se(1)-S(6) 94.12(1), Se(2)-Se(1)-Se(6') 85.88(1), Se2-Se1-Se2' 180, Se2-Se1-Se6 94.12(2), Se2-Se1-Se6' 85.88(2), Se6-Se1-Se6' 180, Se1-Se2-Se3 106.41(2), Se2-Se3-Se4 107.06(2), Se3-Se4-Se5 102.21(2), Se4-Se5-Se6 105.75(3), Se1-Se6-Se5 106.14(2).

Well-formed purple single-crystals of **1** were obtained directly from the original reaction mixture, while greenish-black single-crystals of **2** were grown from a concentrated solution in acetone at r.t. Single-crystal structure determinations of **1** and **2** clearly revealed the presence of separated *catena*-$[S_{12}]^{2-}$ or *spiro*-$[Se_{11}]^{2-}$ dianions, respectively (Figure 1). The terminal S-S bonds in **1** are relatively short at 201.3(2) pm (S1-S2) and 199.6(3) pm (S11-S12), while the inner S-S bonds are in the range of 203.4(3)–207.6(3) pm. A CSD search[15] for crystal structures comprising non-coordinated, unbranched $[S_n]^{2-}$ ions ($n > 6$) revealed four heptasulfides and two octasulfides, in which the terminal S-S bonds are also shorter than the inner S-S bonds (199.5–210.6 pm and 204.0–219.2 pm, respectively). The very recently reported decasulfide dianion $[S_{10}]^{2-}$ exhibits a similar trend: (terminal S-S 201.5(1) and 202.1(1) pm, inner S-S 202.8(1)–207.6(1) pm).[11] The conformation of the $[S_{12}]^{2-}$ ion in **1** is characterised by the rather regular *syn/anti* sequence *anti-anti-anti-anti-syn-syn-syn-syn* with S-S-S-S torsion angles in the ranges 70.7(1) to 93.8(1)° (*anti*) and –73.2(1) to –95.1(1)°) (*syn*). The situation is therefore similar to that in $[S_{10}]^{2-}$, which displays an *anti-anti-anti-anti-anti-syn-syn* sequence and comparable ranges of S-S-S-S torsion angles (72.1(1) to 90.3(1)° and –83.6(1) to –90.8(1)°).[11] *Cyclo*-S_{12}, the second most stable sulfur

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allotrope after *cyclo*-S_8, forms an unstrained twelve-membered ring in the solvate $S_{12}{\cdot}CS_2$ and exhibits only one S-S bond length of 205.4 pm and one torsion angle of 87.2°.[16] There are no significant interactions between the $[S_{12}]^{2-}$ dianions and the PPN^+ cations in **1**.

The structural determination of **2** revealed non-interacting PPN^+ cations and spirocyclic $[Se_{11}]^{2-}$ dianions. The centrosymmetric *spiro*-$[Se_{11}]^{2-}$ dianion in **2** is comprised of two Se_6 rings with typical chair conformations. As found for other salts of $[Se_{11}]^{2-}$,[17-19] the central Se atom (Se1, formally Se^{2+}) is tetra-coordinated in a slightly distorted square-planar fashion. This Se atom engages in 3c-4e bonding as evidenced by the long Se–Se bond lengths of 264.69(4) pm (Se1-Se2) and 266.02(5) pm (Se1-Se6), which are symmetrical in **2,** as well as in the $[PPh_4]^+$ salt.[19] By contrast, these interactions are strongly asymmetrical in the $[N^iPr_4]^+$ salt.[17] For the di-coordinate ring-Se atoms, the bonds are much shorter at 230.71(7)–234.58(7) pm, which is comparable to the values observed for *cyclo*-Se_8.[20]

The crystal structure determination of the dodecasulfide salt $[PPN]_2S_{12}$ (**1**, PPN = $(Ph_3P)_2N$) has confirmed the pioneering work by Seel *et al*., who postulated the formation of $[S_{12}]^{2-}$ more than 30 years ago.[12a] The identification of *catena*-$[S_{12}]^{2-}$ and the very recent characterisation of *catena*-$[S_{10}]^{2-}$ [11] add weight to the suggestion that long-chain polysulfides $[S_n]^{2-}$ (n > 8) should be considered as intermediates in the sulfur ↔ sulfide redox process that occurs in lithium-sulfur batteries, *e.g.* the transformation shown in eqn. (1).[1] The current work also indicates that a long chain polysulfide, *e.g.* $[S_{12}]^{2-}$, may be the source of $[S_3]^{\bullet-}$ in the use of a mixture of sulfur and an alkali- metal carbonate for the synthesis of organosulfur compounds.[5] Finally, the reaction of elemental selenium with potassium carbonate in acetone is a more convenient route to salts of *spiro*-$[Se_{11}]^{2-}$ than previous methods, which involved oxidation of alkali-metal polyselenides (prepared in liquid ammonia) with I_2 in the presence of a large organic cation.[17-19] Significantly, this direct comparison of the outcome of the reactions of potassium carbonate with sulfur or selenium provides a cogent illustration of the predisposition of polyselenides $[Se_n]^{2-}$ (n > 8) to form compact bicyclic structures in preference to the unbranched chains favoured by polysulfides.[10]

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