Electrochemical synthesis of tetrakis[*N*-methylbenzothiazole-2(3*H*)-selone]selenium(2+) tetrafluoroborate: an uncommon dication containing the mixed-valence Se_5 framework

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The electrochemical oxidation of *N*-methylbenzothiazole-2(3*H*)-selone leads to tetrakis[*N*methylbenzothiazole-2(3*H*-selone]selenium(2+) tetrafluoroborate showing an uncommon dication containing a non-cyclic square-planar Se_5 framework; both Mulliken and NBO population analyses explain the relatively long Se–Se bond lengths between the central and the peripheral selenium atoms.

Complexes of divalent selenium and tellurium with bidentate chelating ligands such as dithio- or diseleno-carbamates show that the central atom is always bonded to four sulfur and/or selenium atoms in a trapezoid planar arrangement.[1–4] Two classes of such complexes were distinguished by Bröndmo *et al.*;[1] both classes had two relatively strong and two relatively weak interchalcogen bonds. In the first class, the central atom is bonded to two bidentate ligands, thus determining monomeric complex molecules; in the second class, the complexes can be envisaged as polymers, in which the ligands are bridging and the intermolecular bonds are particularly long. More recently, Se_5 frameworks having geometries close to square-planar have been found in some mixed-valence polychalcogenides and in several complex anions.[4–8] In all the reported structures, the chalcogen(II) atom is coordinated by anionic ligands.

Recently, we reported some interesting compounds obtained by reacting *N*-methylbenzothiazole-2(3*H*)-selone (L) with oxidizing agents such as I_2 and IBr.[9] Now, in an attempt to oxidize L electrochemically,† we have synthesized a compound of formula $[SeL_4][BF_4]_2$ **1**, where the $[SeL_4]^{2+}$ cation can be formally described by analogy with the transition-metal complexes as being formed by a central Se^{2+} cation coordinated by four neutral molecules of L to achieve an almost square-planar geometry of five selenium atoms (Fig. 1).‡ The four benzothiazole molecules are arranged in parallel pairs, two above and two below the plane defined by the five selenium atoms and almost normal to it; their molecular planes are also parallel to the *b* unit-cell axis. Although several cations containing Se_n frameworks are known,[10–12] this is the first example of a non-cyclic square-planar Se_5 fragment which is part of a cation. The four Se–Se distances are very similar in value and are significantly longer than the sum of the covalent radii. These distances are similar to those previously reported for α-$[PPh_4]_2[Se(Se_5)_2]$,[5] β-$[PPh_4]_2[Se(Se_5)_2]$,[5] $[PPh_4]_2[Se(Se_5)_2]$,[6] $[NBu_4]_2[Se(Se_2C{=}C(CN)_2)_2]$,[7] and $Cs_4[Se(Se_5)_3]$,[8] and to the mean values of the trapezoid planar arrangements.[1–3,6] As pointed out above, the five selenium atoms of all previously reported square-planar Se_5 frameworks are part of a neutral molecule or of an anion. In order to explain the long Se–Se distances in the present compound, MO calculations have been carried out on a smaller model system.§ Analysis of the MO orbitals[13–21] shows that the bonds arise from the interactions between the 4s and 4p orbitals of the selenium atoms and have a covalent character. Moreover, both Mulliken and NBO atomic population analyses (see Table 1) show that the central selenium atom bears a small net negative charge, whereas the other selenium atoms are positively charged. The corresponding electronic configurations are $4s^{1.85}$ $4p^{4.31}$ and $4s^{1.83}$ $4p^{3.50}$ for the central and peripheral selenium atoms, respectively. Since the 3d orbitals are completely filled, they do not participate directly in the bonding. The two highest occupied molecular orbitals, that are almost degenerate, are non-bonding orbitals, and are essentially made up of the p atomic orbitals in the molecular plane of the peripheral selenium atoms (see Fig. 2). These two orbitals are responsible for the experimentally observed relatively long interselenium bond lengths. This evidence suggests a pure σ bond between the central and the other selenium atoms, due to the 4s and 4p orbitals. Of course the situation should be different in the real complex, since the methyl groups are a poor representation of the methylbenzothiazole groups. However, we believe that the methylbenzothiazole groups should favour the covalent description of the Se–Se bond, since they can further stabilize the positive charge.

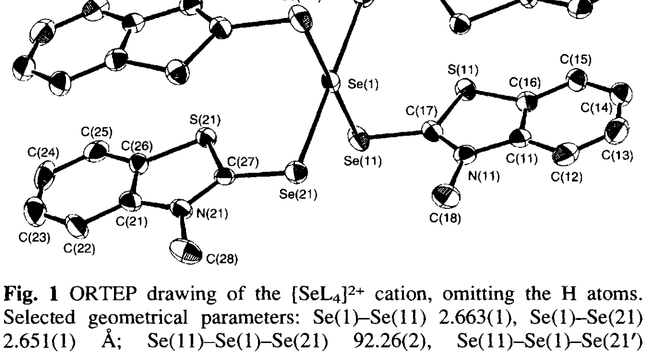
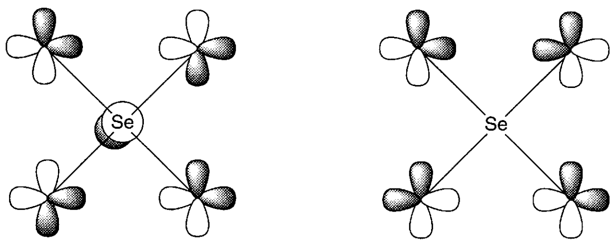


Fig. 1 ORTEP drawing of the $[SeL_4]^{2+}$ cation, omitting the H atoms. Selected geometrical parameters: Se(1)–Se(11) 2.663(1), Se(1)–Se(21) 2.651(1) Å; Se(11)–Se(1)–Se(21) 92.26(2), Se(11)–Se(1)–Se(21′) 87.74(2) °.

On the other hand, these long distances can be explained simply in terms of the VSEPR model by the strong 90°

Table 1 Net charges on the Se_5 framework calculated by Mulliken and NBO atomic population analyses

	Mulliken	NBO
$Se_{central}$	−0.137	−0.188
$Se_{peripheral}$	0.373	0.569
$Se_{peripheral}$	0.346	0.561



HOMO–1
$E = -0.507$ Hartree

HOMO
$E = -0.507$ Hartree

Fig. 2 Picture of the two highest occupied MO orbitals

repulsion between the two axial lone pairs of the central selenium atom and the four Se–Se bond pairs.

Analogous conclusions have been drawn by Kobayashi *et al.*[21] on the basis of NMR and XPS studies carried out on bis(dimethylselenocarbamoyl) triselenide. In particular, the low binding energy of the 3d core level of the central selenium atom indicates that a negative charge rather than a positive one must be developed on this selenium, in agreement with a covalent-bond description for the Se_5 framework.

The possibility of obtaining other cations containing Se_5 or mixed-chalcogen Se_nS_{5-n} frameworks by an electrochemical oxidation, using different substrates and solvents, is now under investigation.

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Footnotes

† Crystals of $[SeL_4][BF_4]_2$ were grown in a standard 50 ml H-cell with a G3 frit separating the anode and cathode compartments. The electrodes used were 0.5 mm Pt wire, of which approximately 1.5 cm were immersed in the solution. The electrolyte was composed of a 0.1 mol dm^{-3} solution of NBu_4BF_4 containing a concentration of 0.01 mol dm^{-3} of *N*-methylbenzothiazole-2(3*H*)-selone (Aldrich, and used without further purification). The electrolysis was conducted using a current of 25 μA. The solvent used was CH_2Cl_2 (Aldrich anhydrous grade). Shortly after the start of the experiment, the solution around the anode began to turn red. Within a few days, well formed pure crystals could be harvested from the anode. These were washed with MeCN.

‡ Crystals of **1** contain $[SeL_4]^{2+}$ cations, located on crystallographic inversion centres and BF_4^- anions in general positions in the unit cell. Interionic contacts are not shorter than the sum of the van der Waals radii; the BF_4^- anions, weakly interacting with the surrounding cation molecules, are affected by high thermal motion and are partially disordered [the highest electron density residuals in the final difference Fourier map (0.9 eÅ^{-3}) are close to the fluorine atoms]. A prismatic crystal with approximate dimensions 0.10 × 0.12 × 0.25 mm was used. The diffraction measurements were carried out on an Enraf-Nonius CAD4 diffractometer at room temperature, using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). Cell dimensions refined from the diffractometer angles of 25 reflections are: a = 10.671(2), b = 14.899(3), c = 13.162(2) Å, β = 107.16(1)°, U = 1999.3(6) Å^3, space group $P2_1/n$, Z = 2, μ = 48.0 cm^{-1}, D_c = 1.94 g cm^{-3}. The diffracted intensities were corrected for Lorentz, polarization, absorption (empirical correction) and for extinction. The structure was solved by direct methods. 3507 unique intensities ($2\theta_{max}$ = 50°) were collected, of which 2036 [with $I > 3\sigma(I)$] were used in the refinement (on F, 246 variables). R = 0.043, R_w = 0.057. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/11.

§ The calculations are based on the Kohn–Sham (KS) approach[13] to the density functional theory as implemented in the Gaussian 92/DFT package.[14] The self-consistent equations were solved within the local density approximation (LDA) using the exchange-correlation potential of Vosko, Wilk and Nusair.[15] Gradient corrected (GC) computations were performed self-consistently by adding the Becke gradient correction to exchange[16] and the Perdew[17] correlation functional to the LDA functional. A double-zeta basis set[18] with the contraction scheme (14, 9, 5)/[8, 5, 3] has been used for selenium, whereas the standard D95 Huzinaga-Dunning basis set[19] has been used for the C and H atoms. In all the computations, the *N*-methylbenzothiazole groups have been replaced by methyl groups with standard geometry. This model molecule has C_s symmetry. Selenium–selenium bond features have been analysed in terms of the natural bond orbital (NBO) scheme.[20] In the framework of the DF approach, these NBOs are given by the opportune transformation of the density matrix obtained by the KS orbitals. It is known that the true KS orbitals (*i.e.* those that would correspond to the exact exchange-correlation potential) are an approximation of the HF orbitals, and their quality must be assessed computationally. In the text, the orbitals coming from the DF approach are referred to simply as orbitals.

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