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N-Heterocyclic carbene stabilized parent sulfenyl, selenenyl, and tellurenyl cations (XH^+, X = S, Se, Te)

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Synthetic and Structural Investigations of Bis(N-alkyl-benzoselenadiazolium) cations

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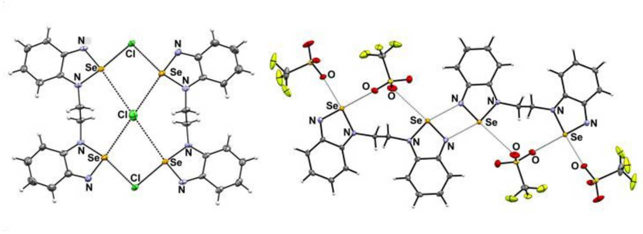
TOC entry

A variety of supramolecular structures is formed by selenadiazolium cations linked by hydrocarbon bridges



Abstract

The synthesis, spectroscopic and structural characterization of bridged dicationic derivatives of benzo-2,1,3-selenadiazoles are reported. The chloride salt of $[H_4C_6NSeN\text{-}CH_2\text{-}CH_2\text{-}NSeNC_6H_4]^{2+}$ crystallized forming a macrocyclic structure in which two cations are bridged by Se···Cl chalcogen bonds (ChBs), with a third chloride at the centre of the macrocycle. The structure of $[1,2\text{-}(H_4C_6NSeN)_2\text{-}C_6H_{10}]Cl_2$ consists of two selenadiazolium cations linked by a chiral cyclohexane and capped by Se···Cl ChBs. The tetrafluoroborate salts of a xylene bridge crystallized in two

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pseudopolymorphs in which the cations form Se···F ChBs in *anti* or *syn* conformations. The triflate salt of ethylene bridged cations dimerize through the formation of the $[Se-N]_2$ supramolecular synthon with Se···O ChBs capping the second selenium atom. In contrast, $[H_4C_6NSeN-CH_2-CH_2-CH_2-NSeNC_6H_4](CF_3SO_3)_2$ only forms Se···O ChBs.

Introduction

The attractive interaction between positively polarized atoms of *p*-block elements and electron-rich Lewis bases, has emerged as an interesting alternative to the ubiquitous hydrogen bonding in supramolecular chemistry. By analogy to halogen bonding[1], the term *chalcogen bonding* (ChB) is now commonly used to denote such interactions when centred on heavy group-16 elements (E= S, Se, Te). Recent advances on chalcogen bonding research[2,3] encompass a wide range of applications in crystal engineering[4-7], catalysis[7-10], anion transport[8,9], anion recognition[10,11], and the assembly of supramolecular capsules[12], polymers[13-15], and macrocycles.[16-20] A particularly interesting example is the development of new organic semiconductors through the formation of S/Se···N ChBs.[21]

The molecules of 1,2,5-chalcogenadiazoles (**1**, **2** in Scheme 1) have been of special interest due to their propensity to associate with Lewis bases, neutral and anionic molecules and themselves through the formation of Ch···N (Ch = S, Se, Te) ChBs.[5,22,23] Within the series, the telluradiazoles form the strongest Ch···N ChBs. These building blocks assemble supramolecular ribbons or dimers, depending on the steric hindrance, thanks to the $[Te–N]_2$ supramolecular synthon.[5] The autoassociation of derivatives of **2c** enables potentially useful optical properties such as second-harmonic generation[24] and chromotropism[25]. However, their moisture sensitivity hampers wide-spread application of the tellurium compounds.

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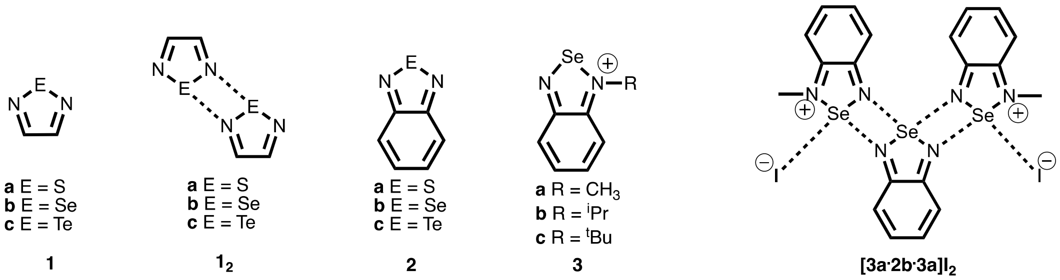

Scheme 1. Chalcogenadiazoles and their *N*-alkyl cations.

The selenium congeners (**1b**, **2b**) form weaker Se$\cdots$N ChBs but these can be strengthened by increasing the electron-withdrawing ability of the nitrogen atom in the antipodal position.[26] This can be achieved by attachment of Lewis acidic groups such as electron-deficient boranes[27], transition metal ions[28,29], or alkyl groups (formally carbocations).[30,31] In the first two cases, the lability of the bond between the nitrogen and the acidic group limits the application of this approach as a general strategy in the construction of supramolecular structures. On the other hand, nitrogen-carbon bonds usually are kinetically stable. Furthermore, the stability towards hydrolysis of the cationic derivatives makes them very attractive as supramolecular building blocks.[30]

In comparison to **1c** and **2c**, the auto-association of **3a** is limited to dimers in the best case. However, pseudo-trimers (e.g. **[3a·2b·3a]I$_2$**), can be formed with the introduction of the neutral heterocycles.[30,32] In order to favor the crystallization supramolecular polymers, we investigated dicationic molecules built by linking two *N*-alkyl selenadiazolium cations (Scheme 2). Here we report the use of hydrocarbon bridges, including a chiral 1,2-cyclohexane bridge, in such dicationic supramolecular building blocks.

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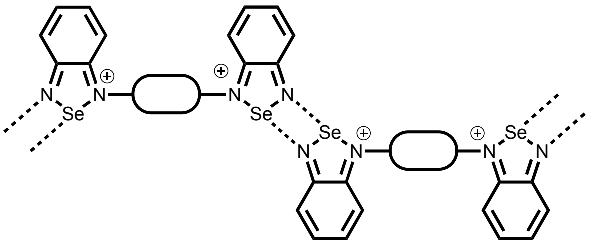
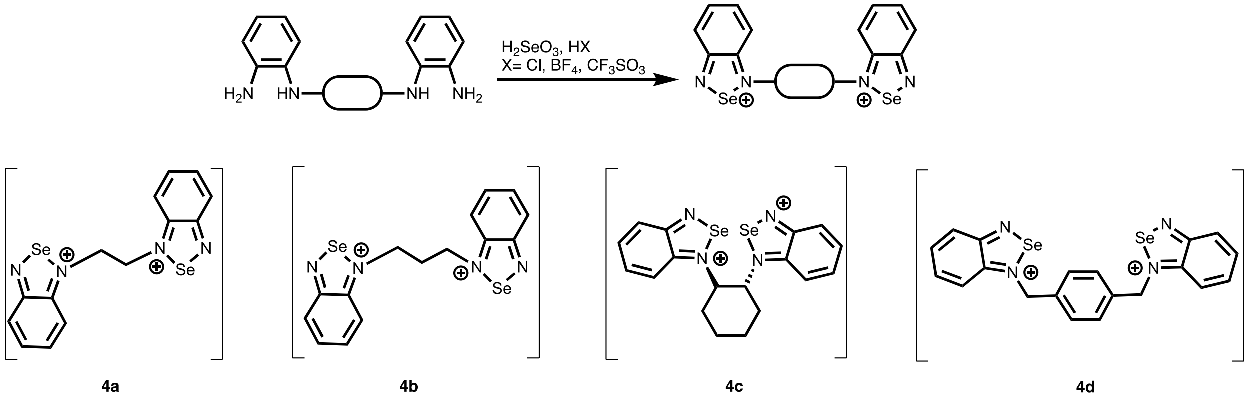


Scheme 2. Proposed supramolecular polymers assembled by of bis(benzo-2,1,3-selenadiazolium) cations.

Results and Discussion



Scheme 3. General approach for the syntheses of bis(benzo-2,1,3-selenadiazolium) cations **4a-d**.

The synthetic methods previously developed for the *N*-alkyl benzo-2,1,3-selenadiazolium cations[25] were adapted to the preparation of bridged cations (**4a-d**, Scheme 3). The most flexible approach is based on the condensation of *N*-alkylated aromatic *ortho*-diamines with selenous acid. For the synthesis of dications, the key precursors are bridged bis(*ortho*-phenylene diamines). Some of those reagents can be prepared by the reaction of phenylenediamine with organo-dihalides, but the most efficient procedures are based on nucleophilic aromatic substitution of 1,2-fluoronitrobenzene with diamines followed by catalytic hydrogenation.[33] The latter method was employed with ethylene diamine, 1,3-diaminopropane, and R,R-1,2-diaminocyclohexane; the first method was used to create a 1,4-xylylenyl-bridged tetraamine. The precursor tetraamines prepared

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with these procedures are vulnerable to oxidization upon exposure to air and ambient light; they were most conveniently isolated and purified as their hydrochlorides by treatment with anhydrous hydrogen chloride. To minimize contamination by their oxidation products, these intermediates were not usually stored, instead they were immediately used to produce salts of the bis(selenadiazolium) cations **4a-d**.

The reactions of the diamines with H_2SeO_3 require an acidic medium; aqueous HCl was used in first instance because the organic reagents were prepared as hydrochlorides. However, as discussed below, halides easily compete with neutral nitrogen atoms to form chalcogen bonds. Salts of the less coordinating BF_4^- and $CF_3CO_2^-$ were obtained using the corresponding acid or by anion exchange. However, not all bridge-anion combinations yielded well-defined products. Only the species that could be conclusively identified and properly characterized are described in this report.

Preparation and spectroscopic characterization of chloride salts. In a typical example, the hydrochloride salt of 1,2-di(*o*-aminophenylamino)ethane reacted with a warm solution of selenous acid in aqueous HCl to yield a dark red precipitate. Recrystallization from ethanol gave analytically pure [**4a**]$Cl_2 \cdot 4H_2O$. The R,R-1,2-cyclohexanediyl and 1,4-xylylenyl bridged molecules were used to synthesize chloride salts of **4c** and **4d**. The identity of the products was verified by X-ray diffraction of their single crystals, the homogeneity of [**4a**]Cl_2 and [**4c**]Cl_2 samples was established by combustion elemental analysis. However, the low solubility of [**4d**]Cl_2 precluded satisfactory purification by recrystallization.

The ^{1}H NMR spectrum of the dications **4a-d** is characterized by resonances of the aromatic protons of the benzoselenadiazolium that range from 7.49–7.96 ppm. The positions of these resonances are comparable to those of the *N*-methyl cations, and appear at slightly lower frequency than

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observed for the isopropyl, *tert*-butyl monocations.**[30]** The same aromatic protons are shifted upfield by 0.15 ppm from that of **2b**. The ESI mass spectra clearly displays the isotopic patterns expected for the 2+ cations (Figure 1).

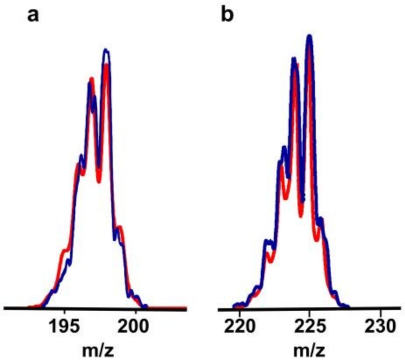

Figure 1. Experimental ESI-HR mass spectrum (blue) and calculated isotropic pattern (red) for: (a) $[C_{14}H_{12}N_4Se]^{2+}$ (**4a**) from [**4a**]$Cl_2 \cdot 4H_2O$; (b) $[C_{18}H_{16}N_4Se]^{2+}$ (**4c**) from [**4c**]$Cl_2 \cdot H_2O$.

Preparation and spectroscopic characterization of the tetrafluoroborate and trifluoromethyl sulfonate salts. Given the strength of binding of halide anions to the chalcogen atom in selenadiazolium cations,**[30]** it was anticipated that Se···Cl$^-$ ChBs would strongly compete with the Se···N ChBs. Attempts were thus made to replace chloride in the initial products with less coordinating species such as BF_4^- and $CF_3SO_3^-$. Preliminary precipitation attempts with $AgBF_4$ failed to produce any solid AgCl, this is likely due to coordination of Ag^+ in spite of the 2+ charge of the cation. Coordination of transition metal ions to cations is rare but has been observed with organic ligands that contain nitrogen donors.**[34]** Successful anion replacement was first achieved in the reaction of [**4a**]Cl_2 with $NOBF_4$ under anhydrous conditions. The by-product, NOCl, is a gas in ambient conditions, which obviates the need for purification workup. The reactions with $NOBF_4$ produced yellow precipitates which were collected and characterized by ^1H and ^{19}F NMR

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spectroscopy. The aromatic proton resonances observed for the tetrafluoroborate salts appear at higher frequency (7.85-8.12 ppm) than those for the chloride salts (7.69-7.96 ppm). The resonances of the protons on the ethylene bridge are found at 5.54 ppm, which is 0.09 ppm above the resonance of that in the chloride salt.

The above anion replacement method is efficient but the overall yield is low. Better results were achieved by adding the tetraamine to a stoichiometric amount of HBF_4 and H_2SeO_3 in solution. The resulting red-orange precipitate was washed with a saturated solution of $NaBF_4$ in ethanol until the remaining acid was removed. The 1,4-xylylenyl derivative [**4d**]$(BF_4)_2$, was prepared in the same way. Recrystallization of this material from acetonitrile gave two polymorphs of [**4d**]$(BF_4)_2$, depending on the concentration of the solution.

As discussed below, because Se···F$^-$ ChBs were observed in the structures of the BF_4^- salts, trifluoromethanesulfonate salts of the dications were prepared with an analogous procedure. The reaction of 1,2-di(*o*-aminophenylamino)ethane and selenous acid in ethanolic trifluoromethanesulfonic acid yielded [**4a**]$(CF_3SO_3)_2$; 1,2-di(*o*-aminophenylamino)propane yielded [**4b**]$(CF_3SO_3)_2$. The resonances of the aromatic protons of [**4a**]$(CF_3SO_3)_2$ range from 7.87 to 8.15 ppm, which are slightly higher in frequency than those of the chloride and tetrafluoroborate salts. The chemical shifts of the same aromatic protons in [**4b**]$(CF_3SO_3)_2$ appear in the same region (7.83 to 8.07 ppm). Because of their modest solubility in DMSO, the ^{77}Se NMR chemical shifts were measured through ^{1}H – ^{77}Se heteronuclear multiple bond correlation (HMBC) experiments. The ^{77}Se values of [**4a**]$(CF_3SO_3)_2$ and [**4a**]$(BF_4)_2$ (1490 and 1482 ppm respectively) appear at 40 ppm higher than that for [**4a**]$Cl_2 \cdot 4H_2O$ (1445 ppm).

Crystal Structures. Full crystallographic data for all new structures are compiled in Table S1 and selected bond distances and angles are compiled in Tables 1 and 2. Although compound [**4a**]Cl_2

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was obtained in pure from the synthesis, single-crystal growth yielded a tetrahydrate. The crystal of [**4a**]$Cl_2 \cdot 4H_2O$ displays a unique molecular arrangement. The dications feature the heterocycles in a *syn* orientation and are organized in pairs bridged by Se···Cl ChBs (2.803, 2.682 Å) conforming a macrocycle-like structure with a third chloride anion at the centre making longer (3.313 and 3.647 Å) contacts with the four chalcogens (Figure 2). The fourth chloride anion sits in the lattice without making any meaningful interatomic contacts.

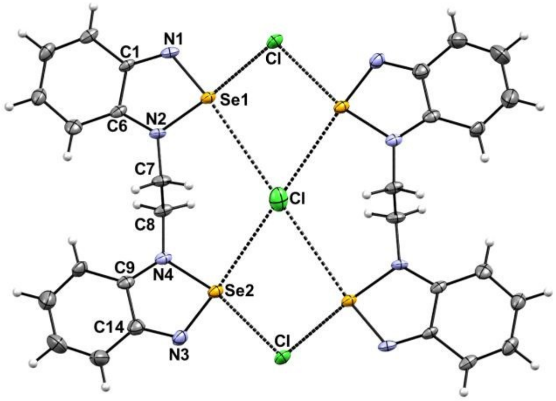

Figure 2. ORTEP and numbering scheme for the asymmetric unit in the crystal structure of [**4a**]$Cl_2 \cdot 4H_2O$. Displacement ellipsoids are shown at the 50 % probability level.

Table 1. Selected distances (Å) and angles (˚) for [**4a**]$Cl_2 \cdot 4H_2O$ and [**4c**]$Cl_2 \cdot H_2O$.

Compound	[**4a**]$Cl_2 \cdot 4H_2O$	[**4c**]$Cl_2 \cdot H_2O$
Se1-N2	1.879 (6)	1.888 (2)
Se1-N1	1.793 (6)	1.768 (2)
Se2-N4	1.867 (6)	1.893 (2)
Se2-N3	1.778 (6)	1.768 (2)
N2-C6	1.341 (8)	1.332 (3)
N2-C7	1.456 (8)	1.480 (3)
N1-C1	1.330 (9)	1.330 (4)
N2-Se1-N1	88.4 (2)	88.55 (1)
Se1-N2-C6	110.6 (4)	110.6 (6)
Se1-N1-C1	111.8 (4)	111.2 (2)

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Compound [**4c**]Cl_2 also crystallized as a hydrate. The asymmetric unit of [**4c**]$Cl_2 \cdot H_2O$ consists of two heterocycles bridged by a 1-(R),2-(R)-substituted cyclohexane ring featuring Se···Cl ChBs with distances of 2.731 Å, which are shorter than found in the monocation (N-hydro-benzo-2,1,3-selenadiazolium chloride) (2.901(1) and 3.075(1) Å). The chirality of the cyclohexane bridge leads to the formation of helical assemblies with a 9° deviation from the normal of the C1, C2, C3, C4 plane in the cyclohexane. (Figure 3) The angle between the two heterocycle planes is much larger (25.5°) than that in the ethylene-bridged dication (4.36°).

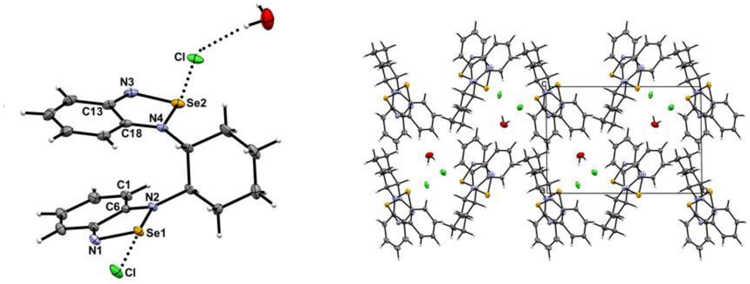

Figure 3. (a) ORTEP and numbering scheme for the asymmetric unit and (b) packing in the crystal structure of [**4c**]$Cl_2 \cdot H_2O$. Displacement ellipsoids are shown at the 50 % probability level.

In the case of the chloride salt of the 1,4-xylylenyl-bridged dication [**4d**]Cl_2, it was not possible to obtain single crystals of the compound because of its low solubility. Attempts to grow crystals by diffusion under several conditions only yielded dendrites that scattered X-rays poorly and thus were unsuitable for a structural determination.

The first polymorph of [**4d**]$(BF_4)_2$ belongs to the $P12_1/n1$ space group and was obtained from acetonitrile. Its asymmetric unit features the dication with an *anti* conformation. Each selenium atom is engaged in a short contact with a BF_4^- anion (Figure 4) the shortest Se···F distance (2.769(1) Å) is shorter than the sum of the van der Waals radii (3.37 Å). A second crystalline phase from this salt, a pseudopolymorph, was obtained from a dilute solution in acetonitrile and includes

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solvent in the lattice ([**4d**]$(BF_4)_2 \cdot CH_3CN$). The sample deteriorated likely due to loss of the solvent and only 85% of the collected data was processed. In this case, the molecular dication structure displays a *syn* conformation that appears to chelate the BF_4^- anion. The Se···F distances are 3.005(8), and 2.914(7) Å.

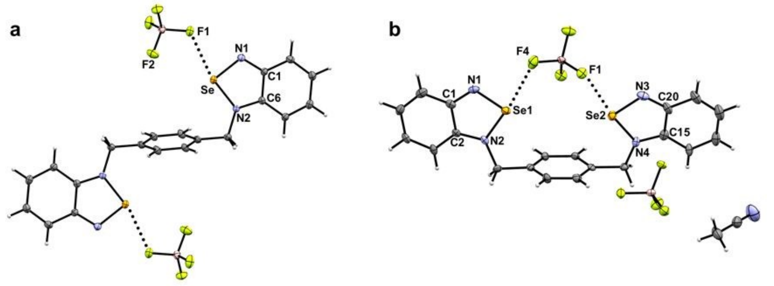

Figure 4. Molecular structures in the crystals of (a) [**4d**]$(BF_4)_2$ and (b) [**4d**]$(BF_4)_2 \cdot CH_3CN$. Hydrogen atoms are omitted for clarity and displacement ellipsoids are shown at 50 % probability level.

The asymmetric unit of [**4a**]$(CF_3SO_3)_2$ (Figure 5) includes two heterocycles bridged by one ethylene molecule and two units of trifluoromethanesulfonate anions. Selected distances and angles are compiled in Table 3. One heterocycle in the dication forms the $[Se{-}N]_2$ supramolecular synthon with a neighbouring cationic heterocycle with Se-N distances of 2.588(2) Å. The same selenium atom also has close contacts with the oxygen atoms of the trifluoromethanesulfonate anions which are sitting above and below the plane of the cationic ring. (3.295(3), 3.319(3), 3.357(3) Å) The selenium atom of [**4b**]$(CF_3SO_3)_2$ features much shorter Se···O ChBs (2.665(1), 2.808(2), 3.137(2) Å) and does not form Se···N ChBs as the trifluoromethanesulfonate anion blocks this site.

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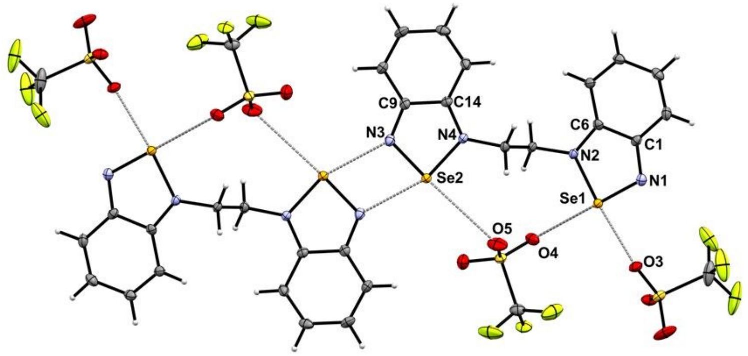

Figure 5. ORTEP and numbering scheme for the asymmetric unit in the crystal structure of [**4a**]$(CF_3SO_3)_2$. Displacement ellipsoids are shown at the 50 % probability level.

Table 2. Selected distances (Å) and angles (°) for [**4d**]$(BF_4)_2$, [**4d**]$(BF_4)_2{\cdot}CH_3CN$, [**4a**]$(CF_3SO_3)_2$ and [**4b**]$(CF_3SO_3)_2$.

Compound	[**4d**]$(BF_4)_2$	[**4d**]$(BF_4)_2{\cdot}CH_3CN$	[**4a**]$(CF_3SO_3)_2$	[**4b**]$(CF_3SO_3)_2$
Se-N1	1.768 (2)	1.757 (3)	1.768 (2)	1.760 (2)
Se-N2	1.833 (1)	1.821 (4)	1.854 (2)	1.843 (2)
Se-N4	1.833 (1)	1.835 (3)	1.838 (2)	1.836 (1)
Se-N3	1.767 (1)	1.756 (4)	1.777 (2)	1.768 (2)
N2-C6	1.341 (2)	1.330 (6)	1.337 (3)	1.349 (2)
N2-C7	1.485 (2)	1.474 (5)	1.469 (3)	1.482 (2)
N1-C1	1.332 (2)	1.342 (6)	1.326 (3)	1.336 (3)
N2-Se1-N1	90.4 (6)	90.5 (2)	89.44 (8)	89.84 (7)
Se1-N2-C6	110.4 (1)	111.3 (3)	110.7 (2)	110.6 (1)
Se1-N1-C1	109.9 (1)	109.8 (3)	110.8 (2)	110.6 (2)

The asymmetric unit of [**4b**]$(CF_3SO_3)_2$ contains a two selenadiazolium heterocycles linked by a –$(CH_2)_3$– chain. The trifluoromethanesulfonate anions are bound to the chalcogen, precluding the formation of Se···N ChBs. The oxygen atoms display short distances to Se (2.685(1), 2.808(2) and 3.137(2) Å), all shorter than the sum of Se and O van der Waals radii (3.47 Å). Similar Se···O ChB distances were observed in the dimer of the N-methyl-benzoselenadiazolium cation (2.823(8) Å).[30]

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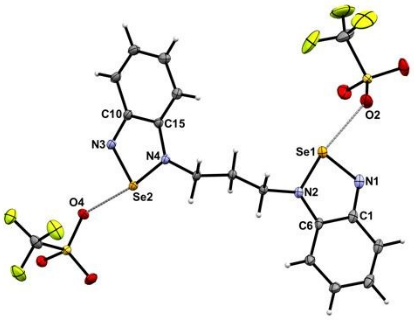

Figure 6. ORTEP and numbering scheme for the asymmetric unit in the crystal structure of (a) [**4b**](CF_3SO_3)$_2$. Displacement ellipsoids are shown at the 50 % probability level.

Experimental

Materials. Selenium dioxide, fluoro-2-nitrobenzene, diamines and other reagents were used as received from commercial suppliers. Anhydrous-grade solvents were used without further purification.

Instrumentation. ^{1}H, ^{13}C and ^{77}Se NMR spectra were recorded on Bruker 200 and Bruker 600 spectrometers at ambient temperature. Chemical shifts are reported in δ values (parts per million) with respect to the resonances of tetramethylsilane for ^{1}H and ^{13}C and with respect to the line of Me_2Se for the chemical shift of ^{77}Se. In the last case, spectra were obtained using ^{1}H-^{77}Se HMBC unless otherwise stated. All vibrational spectra were measured neat by Diffuse Reflectance Infrared Fourier Transform Spectroscopy in a Bio-Rad FTS40 spectrometer with a resolution of 4 cm^{-1} in the 4000–40 cm^{-1} region. Low- and high-resolution electrospray spectral analyses were performed using Micromass GCT spectrometer and a Micromass Quattro Ultima for electron ionization spectra. In each case, the sample was introduced into the ionization chamber in a shortened borosilicate glass capillary on a probe rod. The samples were then heated and the temperature range that displayed the most intense parent ion peaks was used for spectral acquisition. A 70 eV

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electron stream ionized the sample and the positively charged ions were identified by a time-of-flight detector. Elemental analyses were performed by the Science Centre of London Metropolitan University, 29 Hornsey Road, London, UK, N77DD. No melting points are gives as all dication salts decomposed without melting by heating able 150 °C.

All single crystal X-ray diffraction samples were mounted with paratone oil at the tip of a glass fibre installed on a MiTeGen goniometer head and kept under a cold stream of nitrogen while on the diffractometer. Data were collected at 100 K on a Bruker APEX2 diffractometer, using Mo K α radiation ($\lambda = 0.71073$ Å) and outfitted with an Oxford cryostream low-temperature accessory. Ω and ϕ scans were collected in 0.5° steps with a crystal to detector distance of 4.954 cm. The preliminary unit cell parameters were determined using a minimum of 50 frames from three different orientations, and final cell refinement after integration in SAINT.[35] Data were corrected for absorption and scaled using face-indices as well as redundant data in SADABS.[36] Crystal structures were solved using SHELXL and most structures were refined by full-matrix least square of all F2 values with the WinGX package.

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Syntheses of chloride salts

[4a]$Cl_2\cdot 4H_2O$. A neat mixture of fluoro-2-nitrobenzene (1.42 mL, 3.5 mmol) and ethylenediamine (0.5g, 1.7 mmol) was stirred vigorously for 1 hour at 100°C in 25 mL of ethanol. A crystalline solid formed on cooling to room temperature and was separated by filtration. This nitro compound (0.5g, 1.66 mmol) was dissolved in absolute ethanol (30 mL) and Pd/C 10% (50 mg) was added to the solution with stirring. The mixture was placed in a stainless-steel reactor and held under 1 atm of pure H_2. Progress of the reduction reaction was monitored by TLC on silica with an eluent mixture of 10% ethyl acetate in hexanes. Once the starting material was completely consumed, the mixture was filtered through celite and concentrated under vacuum to yield the crude N,N'-bis(2-aminophenyl)ethylenediamine as a brown thick oil. This intermediate was dissolved in anhydrous THF and treated with HCl gas at 0 °C. After 15 minutes, the pale purple solid product was filtered, washed with hexanes and dried under vacuum for 3 h. The hydrochloride salt purified in this way was dissolved in 5 mL HCl_{conc} and mixed with a solution of SeO_2 (2.19 mmol. 4 equiv.) in ethanol A dark red solid formed within minutes and was recrystallized from HCl_{conc} yielding needles of [**4a**]$Cl_2\cdot 4H_2O$. Yield 46 %. ^{1}H NMR (d_6-DMSO): δ (ppm) 7.96(2H, Ar-CH), 7.85(2H, Ar-CH), 7.83 (2H, Ar-CH), 7.69 (2H, Ar-CH), 5.45 (4H, CH_2). ^{1}H-^{77}Se HMBC NMR (d_6-DMSO, 600 MHz): δ (ppm) 1444.9. ^{13}C NMR (d_6-DMSO): δ (ppm) 156.97, 149.52,138.34, 136.69, 129.31,128.30, 116.68(Ar-CH), 52.60 (CH_2). E.A. % calcd. for $C_{14}H_{12}Cl_2N_4Se_2$: C 36.15, H 2.60, N 12.05, found C 36.3, H 2.68, N 12.25.

[4c]Cl_2. Prepared following the procedure described above for [**4a**]$Cl_2\cdot 4H_2O$. Yield 27 %. ^{1}H NMR (d_6-DMSO): δ (ppm) 7.84 (m, 1H, Ar-CH), 7.63 (m, 1H, Ar-CH), 7.43 (m, 1H, Ar-CH), 6.21(m, 1H, Ar-CH, 3.46 (m, 2H, CH_2-cycl) 2.38 (m, 2H, CH_2-cycl), 1.97(m, 2H, CH_2-cycl), 1.83(m, 2H, CH_2-cycl). ^{13}C NMR (d_6-DMSO): δ (ppm) 156.25, 150.52, 136.43, 128.82, 125.00, 117.28 (Ar-

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CH), 66.33, 24.12, 36.49 (($(CH_2)_3$)). E.A. % calcd. for $C_{18}H_{18}Cl_2N_4Se_2$: C 41.64, H 3.49, N 10.79, found C 41.40, H 3.35, N 10.57.

[4d]Cl₂. 1,4-Bis(bromomethyl)benzene (1 g, 3.79 mmol) was dissolved in 35 mL of CH_3CN with *o*-phenylenediamine (2.05 g, 18.9 mmol) and refluxed 4 hours under N_2, after which a white precipitate formed. The solvent was removed under reduced pressure and a 10^{-5} M solution of NaOH was added, this was followed by extraction with CH_2Cl_2 until the pH of the aqueous layer remained constant. The organic layer was dried using Na_2SO_4 and concentrated. The crude material was sublimed at 100°C under reduced pressure to yield (N,N'-bis(2-aminophenyl)-*p*-xylylenediamine) as a dark orange viscous oil. Yield 82 %. ^{1}H NMR (CD_3D, 200MHz): (δ ppm) 7.36 (s, 4H, Ar-H), 6.61, 6.55 (m, 4H, Ar-H), 4.32 (s, 4H, CH_2) ppm. LR ESI-MS: *m/z* 319.2 (M+H) (*Cf.* calc. for $C_{20}H_{22}N_4$ 319.2). The tetraamine (0.989 g, 3.11 mmol) was dissolved in 20 mL of anhydrous CH_2Cl_2 under N_2 and treated with HCl(g) for 15 min until precipitation of a pale-purple solid was complete. Titration with 0.05 M NaOH established that the product obtained was 4-(2-NH_2-C_6H_4-NH-CH_2)-C_6H_4·3HCl. Yield 93%. IR: 3377.21, 2871.60, 2603.85, 2090.36, 2011.76, 1633.05, 1561.82, 1510.17, 1461.45, 1322.50, 1155.30, 1137.52 cm^{-1}. HR ESI-MS: *m/z* 319.1923 (M+H) (*Cf.* calc. for $C_{20}H_{22}N_4$ 319.1916). The hydrochloride salt (0.409 g, 0.96 mmol) was dissolved in 40mL 1:1 v/v 10% HCl/EtOH. H_2SeO_3 (0.308 g, 2.39 mmol) was dissolved in 4 mL of the same solvent and added to the mixture. The solution turned red and produced a yellow precipitate. The solid product, [**4d**]Cl_2, was isolated by filtration and dehydrated by suspending it in an ethanol-toluene mixture and heating to reflux though a column of activated alumina. Yield 61 %. ^{1}H NMR (d_6-DMSO, 600MHz): (δ ppm) 7.95 (d, 2H, Ar-H), 7.83 (m, 4H, Ar-H), 7.67 (m, 2H, Ar-H), 7.48 (s, 4H, Ar-H), 6.14 (s, 4H, CH_2) ppm. ^{13}C NMR (d_6-DMSO, 600MHz): (δ ppm) 158.98, 149.53, 136.69, 136.32, 129.31, 128.73, 125.40, 116.68, (Ar-CH) 53.60 (CH_2) ppm. ^{1}H-

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^{77}Se HMBC NMR (d$_6$-DMSO, 600MHz): (δ ppm) 1445.8. IR: 3055.60, 2970.40, 2937.30, 2793.36, 2721.35, 2637.11, 1977.05, 1955.18, 1837.26, 1810.53, 1714.29, 1607.43, 1530.10, 1504.74, 1423.52, 1323.22, 1163.82 cm-^{1}. LR ESI-MS: *m/z* 235.7 (M^{2+}) (*Cf.* calc. for $C_{20}H_{16}N_4Se_2^{2+}$ 236.5), 506.9 (M-Cl) (*Cf.* calc. for $C_{20}H_{16}N_4Se_2Cl^+$ 506.9). No satisfactory combustion elemental analysis could be obtained for this product.

Syntheses of tetrafluoroborate salts

[4a](BF$_4$)$_2$: (a) A small sample of [**4a**]Cl$_2$ (0.03g, 0.06 mmol) was treated with $NOBF_4$ (0.015g, 0.12 mmol) in anhydrous acetonitrile under N_2. The reaction mixture was stirred for 2 hours and the solvent was removed under vacuum to give yellow powder. Yield 6%. (b) Prepared in a polypropylene test tube following the procedure described above for [**4a**]Cl$_2$·4H$_2$O, with 48% wt. HBF_4 in water instead of HCl$_{conc}$. Yield 30 % ^{1}H NMR (d$_6$-DMSO): δ (ppm) 8.05 (m, 1H, Ar-CH), 7.94 (m, 1H, Ar-CH), 7.77(m, 1H, Ar-CH), 7.50(m, 1H, Ar-CH), 6.26 (d, 2H, CH$_2$). ^{77}Se NMR (d$_6$-DMSO, 600 MHz) δ (ppm): 1481.6. ^{13}C NMR (d$_6$-DMSO): δ (ppm) 156.93, 150.07, 137.93, 130.29, 125.57, 116.42(Ar-CH), 53.5 (CH$_2$). No satisfactory combustion elemental analysis could be obtained for this product.

[4d](BF$_4$)$_2$. (N,N'-bis(2-aminophenyl)-*p*-xylylenediamine) (0.234 g, 0.735 mmol) was suspended in 9 mL of CH_3OH in a polypropylene test tube. 48% wt. HBF_4 in water (1.15 mL, 7.17 mmol) was added to the suspension, dissolving immediately all solids to form a brown solution. H_2SeO_3 (0.235 g, 0.185 mmol) was dissolved in 2 mL of CH_3OH and added to the solution. The mixture turned red and a redish-orange precipitate was formed. After 1 hour, the mixture was centrifuged, the liquid was decanted, and the solid was washed with a saturated solution of $NaBF_4$ in EtOH until the pH of the solution was no longer acidic. This was followed by a wash with EtOH, then a final wash with anhydrous ether and allowed to dry under atmosphere. The resulting orange

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powder was recrystallized from CH_3CN and the final product consisted of orange needle-like crystals. Yield 66 %. ^{1}H NMR (d_6-DMSO, 600 MHz): δ (ppm) 8.05 (d, 2H, Ar-H), 7.93 (m, 4H, Ar-H), 7.77 (m, 2H, Ar-H), 7.50 (s, 4H, Ar- H), 6.26 (s, 4H, CH_2) ppm. ^{13}C NMR (d_6-DMSO, 600MHz) (δ ppm): 53.45, 116.42, 125.57, 128.64, 130.29, 135.91, 137.39, 150.08, 156.93 (Ar-CH). ^{1}H-^{77}Se HMBC NMR (d_6-DMSO, 600MHz): δ (ppm) 1481.5. ^{19}F NMR (d_6-DMSO, 200MHz) (δ ppm): -151.5 ppm. IR: 3606.23, 3519.00, 3104.46, 2045.80, 3022.69, 2384.48, 2106.00, 1969.36, 1822.20, 1606.87, 1532.31, 1396.54, 1319.03, 1115.62 cm-^{1}. LR ESI-MS: *m/z* 236.2 (M^{2+}) (*Cf.* calc. for $C_{20}H_{16}N_4Se_2^{2+}$ 236.5), 559.3 (M-BF_4) (*Cf.* calc. for $C_{20}H_{16}N_4Se_2BF_4^+$ 559.0). E.A. % calcd. for $C_{20}H_{16}B_2F_8N_4Se_2$: C 37.31, H 2.50, N 8.70, found C 37.13, H 2.85, N 8.59. The pseudopolymorph [**4d**]$(BF_4)_2\cdot CH_3CN$ formed yellow crystals by slow evaporation of an acetonitrile solution.

Preparation of trifluoromethylsulfonate salts. Triflic acid (0.5 M in EtOH) was added dropwise to a mixture of the corresponding tetraamine and one equivalent of SeO_2 in anhydrous ethanol. Red powders formed over 24 hours, were recovered by filtration and recrystallized from acetonitrile. The identity of the products was confirmed by single-crystal X-ray diffraction but satisfactory elemental analyses could not be obtained after repeated attempts.

[4a]$(CF_3SO_3)_2$: Yield 38 % ^{1}H NMR (d_6-DMSO): δ (ppm) 8.15(m, 1H, Ar-CH) 8.08(m, 1H, Ar-CH), 7.87 (m, 2H, Ar-CH). 5.18 (m, 4H, CH_2) ^{13}C NMR (d_6-DMSO) δ (ppm): 156.57, 151.11, 137.35. 130.35, 125.53, 116.33 (Ar-CH), 51.30 (CH_2). ^{1}H-^{77}Se HMBC NMR (d_6-DMSO, 600 MHz): δ (ppm) 1490.0.

[**4b**]$(CF_3SO_3)_2$: Yield 30 % ^{1}H NMR (d_6-DMSO): δ (ppm) 8.07 (m, 3H, Ar-CH), 7.83 (m, 1H, Ar-CH), 5.20 (t, 2H, CH_2). 2.60 (p, 1H, CH_2). ^{77}Se NMR (d_6-DMSO, 600 MHz) δ (ppm) 1486.3. ^{13}C

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NMR (d_6-DMSO) δ (ppm): 156.65, 150.63, 137.11, 130.23, 125.0 116.15, (Ar-CH), 48.68 (CH_2), 33.77 (CH_2), 30.06 (CH_2).

Conclusions

The efficient synthetic route previously developed for the *N*-alkyl benzo-2,1,3-selenadiazolium cations was readily adapted to the preparation of a variety of bis(benzoselenadiazolium) cations linked by a variety of hydrocarbon groups that included alkyl chains, a 1,2-cyclohexanediyl, and 1,4-xylylenyl bridges. As anticipated, the dications have a strong affinity for anions; chloride is strongly associated by chalcogen bonding in the solid state. The chlorides were replaced with less coordinating anions such as tetrafluoroborate and trifluoromethanesulfonate in an attempt to promote the formation of Se···N ChBs and the $[Se\text{-}N]_2$ supramolecular synthon. The strategy worked in part in the case of [**4a**]$(CF_3SO_3)_2$, with the formation of dimers in the crystal structure. The selenium atom in the cations most frequently acted as a chalcogen-bond donor towards the fluorine atoms of the tetrafluoroborate and oxygen atoms of the trifluoromethanesulfonate anions. While these anions do interfere with the formation of Se···N ChBs, the resulting structures (e.g. the macrocyclic formed by [**4a**]$Cl_2{\cdot}4H_2O$) offer opportunities for the design of new supramolecular architectures. Further, the crystal structures suggest that the chalcogen-bonding donor ability of these dicationic species could also be applied in anion sensing and catalysis.

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Conflicts of Interest. There are no conflicts to declare.

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