

PAPER

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rsc.li/daltonPolydentate chalcogen bonding: anion trapping
with a water-stable host compound carrying
Se–CF₃ functions†J. Louis Beckmann,^a Natalia Tiessen,^b Beate Neumann,^a
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Bidentate and tetradentate chalcogen bonding host systems with SeCF₃ functions as σ -hole donors in close proximity at the alkyne functions of 1,8-diethynylanthracene and its *syn*-dimer were prepared in quantitative yield by tin-selenium exchange reactions of the corresponding trimethylstannyl precursors with ClSeCF₃. The bidentate system shows chalcogen bonding interactions with THF, but does not bind halide ions. The tetradentate system cooperatively chelates chloride, bromide and iodide ions with its four C \equiv C–SeCF₃ units by rotating the four σ -holes towards the halide ion. The structures of these halide ion adducts were determined by X-ray diffraction. The hydrobromide and -iodide salts of the ethyl derivative of Schwesinger's phosphazene superbase served as halide salts with very weakly coordinating cations.

Introduction

Poly σ -hole host compounds with the ability to cooperatively bind nucleophiles can be more active than their monodentate derivatives because they benefit from a comparable effect to the chelate effect which is well known for polydentate donor ligands.^{1–6} Preorganization of the host compound can further enhance the binding abilities.^{7,8} Consequently, such compounds are of great interest for processes such as catalysis,^{8–10} anion recognition in host–guest chemistry^{11–13} or anion transport.^{14–16} Halogen bonding^{17,18} is the best known member of the family of σ -hole interactions, but in recent years compounds utilizing pnictogen or chalcogen bonding have come to the fore.^{15,16,19–24} Since heavier and thus more easily polarizable atoms are typically better σ -hole donors, most chalcogen bonding systems contain selenium or tellurium.^{6,22} However, there are as well some efficient host systems featuring sulfur.^{25–27} The σ -holes can become stronger lone-pair acceptors by using cationic σ -hole functions^{11,13,24} or by attaching perfluorinated substituents (typically polyfluorinated arenes)^{2,28} or cationic heterocycles.^{4,5,27} For example,

Te(C₆F₅)₂ has been shown to be a more potent catalyst compared to Se(C₆F₅)₂ for Reissert-type reactions with an halide-abstraction as a rate-limiting step, and Sb(C₆F₅)₂Ph outperforms Sb(C₆F₅)Ph₂.²⁸ By choosing a suitable organic backbone, the directionality of multiple σ -hole donor sites can be predetermined to achieve both cooperativity and selectivity. Although the application of cooperative chalcogen bonding is only partially explored, there are some impressive bidentate examples that demonstrate intriguing new possibilities for anion binding and catalysis.

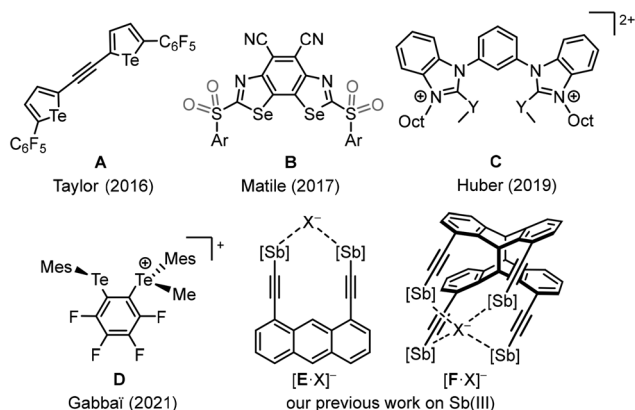
For example, Taylor *et al.* were able to demonstrate the advantages of the bidentate system **A** over a similar monodentate host.² Matile's benzodiselenazoles **B** have conformationally immobilized σ -holes on the selenium atoms, making systems like **B** potent catalysts.²⁶ Hosts such as **C** of Huber and co-workers use sulfur or selenium and were used as cationic chalcogen bonding systems in the activation of neutral compounds.²⁷ Gabbaï introduced the also cationic host **D**, in which the catalytic activity is enhanced by the presence of a telluronium function (Scheme 1).²⁴

It is evident, that the design of the host system is of major importance for the activity of the respective compound. Recently, we have established diethynylanthracene²⁹ and its *syn*-photodimer¹ as potent organic backbones for bi- and tetradentate pnictogen bonding by attaching C \equiv C–Sb(C₂F₅)₂ functions. They can cooperatively bind various nucleophiles such as chalcogenides or halide ions, and the tetradentate host **F** has been shown to clearly outperform the bidentate system **E**.^{1,29} Two major drawbacks of these host systems are their high sensitivity towards moisture and the steric overcrowding in the tetradentate host **F**. Therefore, we have here applied the

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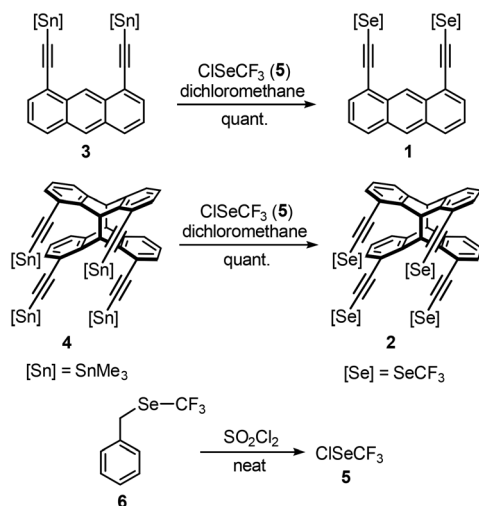
Scheme 1 Mono- and bidentate chalcogen bonding host systems and complexes of our pnictogen bonding host systems investigated previously (Ar = C₆H₄tBu; Y = S, Se; X[−] = Cl[−], Br[−], I[−]; [Sb] = Sb(C₂F₅)₂).

concept of chalcogen bonding to these backbones by attaching C≡C–SeCF₃ functions, thus avoiding steric repulsion while precluding decomposition by hydrolysis.

Results and discussion

The selanyl host compounds **1** and **2** were synthesized by reacting the stannylated precursors **3**³⁰ and **4**³¹ with ClSeCF₃ (**5**, Scheme 2). This was synthesized according to literature³² by chlorinating benzyltrifluoromethyl selenide (**6**)³³ with SO₂Cl₂. The removal of SO₂ was achieved by isothermal distillation, but this purification is not necessary since the reaction of **5** with the stannylated precursors was found to be unperturbed by SO₂ and an excess of **5**.

To get a first indication of the σ-hole donor activity, we purified **5** (m.p. ≈ −100 °C) in order to determine its solid state structure by *in situ* crystallization and X-ray diffraction (Fig. 1).



Scheme 2 Synthesis of selanyl chloride **5** and exchange reaction to afford the monomeric host system **1** and dimeric host system **2**.

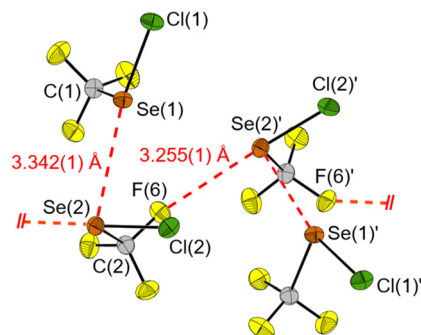


Fig. 1 Molecular structure of **5** in the solid state. To emphasize the infinite chain structure, additional molecules marked with ' are depicted, which were generated by symmetry (+x, 3/2 − y, 1/2 + z). The red dotted lines mark Se...F distances below the sum of van der Waals radii.³⁵ Ellipsoids are set at 50% probability. Selected distances [Å] and angles [°]: Se(1)–C(1) 1.966(2), Se(2)–C(2) 1.967(2), Se(1)–Cl(1) 2.167(1), Se(2)–Cl(2) 2.151(1); C(1)–Se(1)–Cl(1) 94.1(1), C(2)–Se(2)–Cl(2) 94.8(1), Cl(1)–Se(1)–Se(2) 167.8(1), Cl(2)–Se(2)–F(6)' 177.5(1).

There are two independent molecules in the asymmetric unit. One of them forms infinite chains of intermolecular σ-hole interactions (Se(2)⋯F(6)). The other molecules are laterally connected to this chain by Se...Se-type chalcogen bonding interactions, where Se(1) acts as a σ-hole donor and Se(2) as a lone pair donor.

The tin compounds **3** and **4** were reacted with **5** analogously to a protocol of a tin-selenium exchange reaction,³⁴ affording the bi- and tetradentate chalcogen bonding host systems **1** and **2** in quantitative yield. Since **5** was applied neat, the workup to obtain a product of reasonable purity consisted only of removing the excess of **5** as well as the generated chlorotrimethylstannane under reduced pressure. This synthetic protocol allows for a simple and straightforward functionalization with C≡C–SeCF₃ units, which should be readily transferable to other polyalkynes.

The solid state structures of **1** and **2** were determined by single crystal X-ray diffraction (Fig. 2). In both structures, there is approximately a right angle between the alkyne and the trifluoromethyl group (C–Se–C^F angles between 94.4(1)° and 96.8(1)°), which also implies a right angle between the alkyne and the direction of the σ-hole on each selenium atom. Since the direction of the σ-hole can change by rotating along the alkyne axis, all four σ-holes in **2** can point right at the central cavity, making **2** a tetradentate host system. Also of interest are the Se...F distances, which are shorter than the sum of their van der Waals radii ($\sum d_{\text{vdw}}(\text{Se}, \text{F}) = 3.37 \text{ Å}$),³⁵ as they indicate attractive interactions.

There are two remarkably short intramolecular Se...F contacts that indicate chalcogen bonding interactions. These two are contacts between the fluorine atoms of a CF₃ group and the selenium atoms of neighboring SeCF₃ functions. They show some directionality by adopting F...Se–C^F angles of 164.8(2)° and 158.3(1)°. The relatively large deviations from linearity allow these to be classified as weaker chalcogen

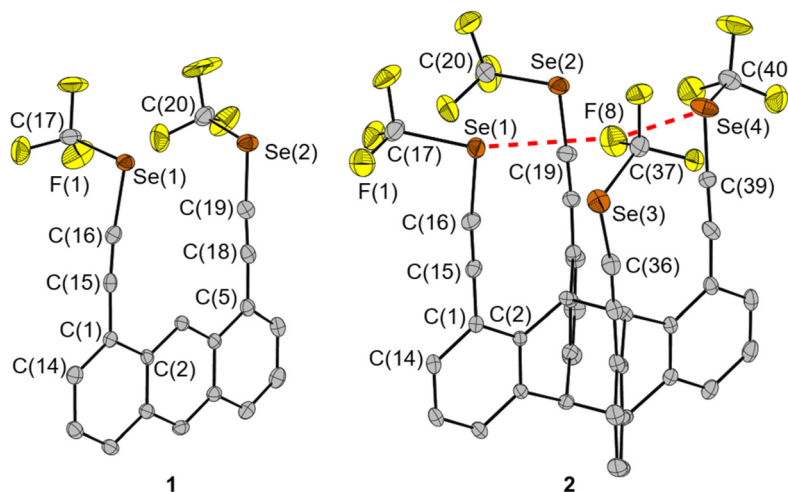


Fig. 2 Molecular structures of **1** and **2** in the solid state. Hydrogen atoms and, in the case of **2**, solvent molecules (benzene) and minor occupied disordered parts are omitted for clarity. The red dotted lines mark Se...F distances below the sum of van der Waals radii.³⁵ Ellipsoids are set at 50% probability. Selected distances [Å] and angles [°] of **1**: Se(1)...Se(2) 4.396(1), Se(1)–C(17) 1.960(4), Se(1)–C(16) 1.824(3), Se(2)–C(20) 1.954(4), Se(2)–C(19) 1.829(3); C(14)–C(1)–C(15) 121.2(3), C(2)–C(1)–C(15) 118.4(2), C(1)–C(15)–C(16) 174.2(3), C(15)–C(16)–Se(1) 173.4(3), C(16)–Se(1)–C(17) 96.3(1); of **2**: Se(1)...F(8) 3.196(2), Se(4)...F(8) 3.296(2), Se(1)...Se(2) 4.217(2), Se(2)...Se(4) 3.680(2), Se(3)...Se(4) 5.769(1), Se(1)...Se(3) 3.892(2); C(16)–Se(1)–C(17) 96.8(1), C(19)–Se(2)–C(20) 94.4(1), C(36)–Se(3)–C(37) 95.6(6), C(39)–Se(4)–C(40) 95.2(3), F(8)–Se(1)–C(17) 164.8(2), F(8)–Se(4)–C(40) 158.3(1).

bonding interactions.³⁶ On a larger scale, **1** forms staggered layers caused by aryl stacking interactions, while molecules of **2** arrange back-to-back to form alternating layers of perfluorinated SeCF₃ groups and organic backbones.

One of our goals was to improve the stability of σ -hole host systems compared to the previously reported bis- and tetrastibanyl host systems, which are highly sensitive to air and moisture. In fact, the selanyl compounds **1** and **2** proved to be stable when stored for at least six months exposed to air and moisture. Solutions of the compounds can even be heated in the presence of concentrated aqueous hydrochloric acid or sodium hydroxide solution without showing decomposition or hydrolysis (see ESI† more information).

By crystallizing compound **1** from THF, we obtained structural insight into the dimer [1:2 THF]₂ by X-ray diffraction (Fig. 3). Here, all four Se...O distances are below the sum of the van der Waals radii ($\sum d_{\text{vdW}}(\text{Se}, \text{O}) = 3.42 \text{ Å}$),³⁵ confirming the donation of both lone pairs of each oxygen atom into one of the two σ -holes of each selenium atom. The Se...O distances associated with the σ -holes opposite to the CF₃ groups are shorter than those opposite to the alkyne groups, demonstrating that the extremely electron-withdrawing CF₃ groups to induce a “deeper” σ -hole and thus a stronger chalcogen bonding interaction. In addition, the O...Se–C^F and O...Se–C^{alkyne} angles are approximately linear (ranging from 172.3(1)° to 177.0(1)°), further indicating typical features of chalcogen bonding.^{6,20}

The next step was to demonstrate the ability of the compounds to bind equimolar amounts of halide ions (Scheme 3). Neither the selanyl compounds **1** or **2** nor the cation of the corresponding halide salt showed any significant shift in the ¹H, ¹⁹F, ³¹P or ⁷⁷Se NMR spectra, thus there is no clear evidence for the existence of an interaction from NMR spec-

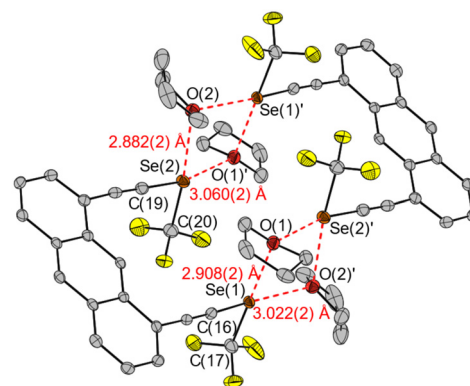


Fig. 3 Molecular structure of [1:2 THF]₂ in the solid state. Hydrogen atoms are omitted for clarity. The red dotted lines mark Se...O distances below the sum of van der Waals radii.³⁵ Ellipsoids are set at 50% probability. Atoms marked with ' are generated by symmetry (1 – x, 1 – y, 1 – z). Selected distances [Å] and angles [°]: Se(1)...Se(2) 4.782(1), Se(1)–C(16) 1.844(3), Se(1)–C(17) 1.969(3), Se(2)–C(19) 1.838(3), Se(2)–C(20) 1.972(3); C(16)–Se(1)–C(17) 92.7(1), C(19)–Se(2)–C(20) 93.0(1), C(16)–Se(1)–O(2') 177.0(1), C(17)–Se(1)–O(1) 172.3(1), C(19)–Se(2)–O(1') 165.0(1), C(20)–Se(2)–O(2) 172.9(1), Se(1)–O(1)–Se(2') 79.5(1), Se(2)–O(2)–Se(1') 80.6(1).

troscopy in solution. Changing the concentration did also not increase this chemical shift difference and the solvent cannot be varied at will due to the limited solubility of the compound. Because the overall shifts are so small (¹H, ¹⁹F and even ⁷⁷Se), it was not possible to determine an association constant *K*_a from the binding isotherms, as we did for the antimony systems in our previous work.

Consequently, we attempted to obtain structural evidence. However, the production of single crystals suitable for X-ray





enium atoms in a roughly rectangular planar fashion. Fig. 4 shows the structure of $[2\cdot\text{Cl}]^-[\text{PPh}_4]^+$, which is similar to that of $[2\cdot\text{Cl}]^-[\text{7}\cdot\text{H}]^+$, which is why the latter is described in the ESI.† The unusual coordination geometry found in the $[2\cdot\text{X}]^-$ anions is comparable to the halide ion adducts of the tetrastibanyl compound reported previously by us.¹ However, the tetrastibanyl compound **2** seems to be better suited for the chelation of halide ions in its central cavity, since the comparably small $\text{C}\equiv\text{C}-\text{Se}(\text{CF}_3)$ units are much more sterically unhindered than the larger $\text{C}\equiv\text{C}-\text{Sb}(\text{C}_2\text{F}_5)_2$ units. Due to the ability of the $\text{C}\equiv\text{C}-\text{Se}(\text{CF}_3)$ units to rotate about the $\text{C}\equiv\text{C}$ -axis, the σ -holes of each selenium atom are directed right towards the centrally chelated halide ion in all three adducts, resulting in collinear $\text{X}\cdots\text{Se}-\text{C}^{\text{F}}$ motifs (angles vary between $171.2(3)^\circ$ and $178.3(1)^\circ$). The four trifluoromethyl groups are oriented outward, forming a cross with the halide ion in their center. In each structure, the halide ion is near the geometric center of the four selenium atoms ($d(\text{X}\cdots\text{Se}_4\text{-centroid})$ Cl: 0.395(1), Br: 0.393(1), I: 0.438(1) Å). Each $\text{X}\cdots\text{Se}$ distance is below the respective sum of the van der Waals radii ($\sum d_{\text{vdW}}(\text{Se},\text{X})$: Cl = 3.65, Br = 3.73, I = 3.88 Å),³⁵ which also confirms four attractive σ -hole interactions. In contrast to the $\text{Sb}-\text{C}^{\text{F}}$ bonds in the tetrastibanyl compound,¹ we observed no significant stretching of the $\text{Se}-\text{C}^{\text{F}}$ bonds due to an electron donation into the $\sigma^*(\text{Se}-\text{C})$ orbitals.

For the adducts $[2\cdot\text{Br}][\text{7}\cdot\text{H}]$ and $[2\cdot\text{I}][\text{7}\cdot\text{H}]$, small occupancies of OH^- ions (23% and 25%) at the halide positions were observed in the single crystals by X-ray diffraction. This is most likely due to traces of $[\text{7}\cdot\text{H}]\text{OH}$ in the bromide and iodide salts used, but it appears that these OH^- ions are preferentially incorporated into the crystals rather than the mostly microcrystalline or amorphous bulk material of the adducts. No such problems were encountered for $[2\cdot\text{Cl}][\text{7}\cdot\text{H}]$ (which is described in the ESI†).

Conclusions

In essence we have demonstrated a quantitative-yielding approach to a bidentate and the first tetradentate chalcogen bonding host system through a tin-selenium exchange reaction with ClSeCF_3 . The introduction of SeCF_3 groups into molecules is of particular interest for material or life sciences and can be achieved by various methods,³⁹ but such a tin-selenium exchange reaction has only been reported for PhSeCl .³⁴

The ability of the SeCF_3 group to function as a chalcogen bonding donor is already evident in the molecular structures of both the free host **2** and ClSeCF_3 in the form of intermolecular $\text{Se}\cdots\text{F}$ and $\text{Se}\cdots\text{Se}$ contacts. The bidentate system **1** forms an adduct with THF, $[\text{1}\cdot\text{2 THF}]_2$, in which **1** uses of both types of its σ -holes. Remarkable NMR shifts of the host-guest complexes could not be observed in the ^1H , ^{19}F , ^{31}P or ^{77}Se NMR spectra, but the molecular structures for a series of halide adducts of the type $[2\cdot\text{X}]^-$ clearly demonstrated the affinity of the tetradentate host for anionic guests. Advantageous in this context was the use of halide salts of extremely weak coordinating cations, which we found in the

hydrohalides of $[\text{7}\cdot\text{H}]\text{Br}$ and $[\text{7}\cdot\text{H}]\text{I}$ of the Schwesinger base $[(\text{Et}_2\text{N})_3\text{PN}]_3\text{PN}^t\text{Bu}$ (**7**). In the halide adducts, **2** aligns all four σ -holes of its $\text{C}\equiv\text{C}-\text{SeCF}_3$ units toward the trapped central halide ion, forming unique planar Se_4X motifs. All $\text{X}\cdots\text{Se}-\text{CF}_3$ chalcogen bonding units are linear and the $\text{X}\cdots\text{Se}$ distances are less than the sum of van der Waals radii. Although there is evidence that the σ -holes at the opposite of alkyne substituents are more activated than those opposite of CF_3 groups,⁴⁰ in our system only those towards CF_3 groups are addressed, probably due to the cooperative effects. Because the compounds are stable in the presence of water, air, and even strong aqueous acids, they have potential for applications in the fields of catalysis and sensing. Initial experiments have shown a catalytic activity of these compounds for the transfer hydrogenation of quinoline derivatives with Hantzsch ester, a common benchmark reaction for such σ -hole compounds.^{25,26}

Author contributions

J. L. Beckmann: investigation, methodology, validation, visualization, writing (original draft), N. Tiessen: investigation (supporting synthesis), B. Neumann: investigation (SCXRD), H.-G. Stammer: investigation (SCXRD), N. W. Mitzel and B. Hoge: funding acquisition, project administration, supervision, reviewing and editing.

Data availability

The data published in this contribution are available as ESI,† submitted with the manuscript.

Conflicts of interest

There are no conflicts to declare.

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