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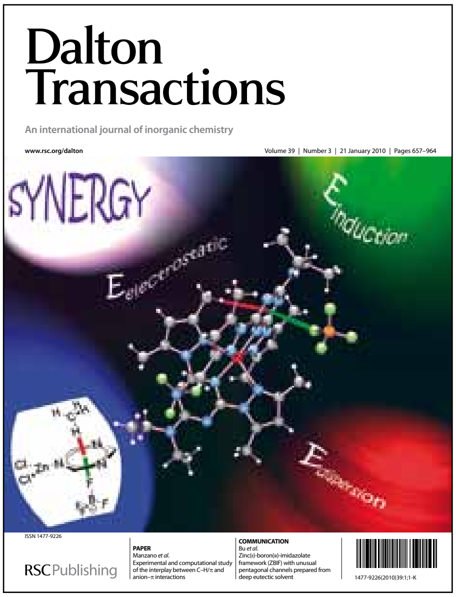

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ARTICLE TYPE

Structural isomerism in (p–XC_6H_4)$SeCl_3$ and (p–XC_6H_4)$SeBr_3$ (X = F, Cl) compounds. Co–crystallisation of *cis*– and *trans*– dimeric forms of (p–ClC_6H_4)$SeCl_2$(μ–Cl)$_2$(p–ClC_6H_4)$SeCl_2$. A new structural modification for the "PhSeBr" reagent, $Ph_2Se_2Br_2$, containing an elongated Se–Se bond.‡

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A series of di(*para*–halophenyl)diselenides, (p–$XC_6H_4)_2Se_2$ (X = F, Cl) have been reacted with three equivalents of SO_2Cl_2 or Br_2, leading to the formation of selenium(IV) $RSeX_3$ compounds. The structures of (p–FC_6H_4)SeX_3 (X = Cl, Br) have been determined, and both exhibit a dimeric $RSeX_2(\mu$–$X)_2RSeX_2$ structure consisting of two "saw–horse" (p–FC_6H_4)SeX_3 units linked by two halide bridges, with an overall square pyramidal geometry at selenium. In both structures all the selenium and halogen atoms are planar, with both aryl rings located on the same side of the Se_2X_6 plane (*cis*– isomer). The structure of (p–ClC_6H_4)$SeCl_3$ also adopts a planar dimeric structure, however both *cis*– and *trans*–dimeric molecules are co–crystallised in the unit cell. In contrast, the structure of (p–ClC_6H_4)$SeBr_3$ adopts a folded *cis*–dimeric structure due to steric constraints. Secondary Se···X interactions to the "vacant" sixth coordination site at selenium are a feature of most of these structures, but are most prominent in the folded structure of (p–ClC_6H_4)$SeBr_3$. A re–examination of the PhSeBr/$PhSeBr_3$ system resulted in the isolation of crystals of a second structural form of "PhSeBr". The structure of $Ph_2Se_2Br_2$ consists of two PhSeBr units linked by an elongated Se–Se bond of 2.832(4) Å, and longer secondary Se···Br interactions of 3.333(4) Å to form a chain structure. Further weak Se···Br and Br···Br interactions are present, which form loosely linked rippled sheets of selenium and bromine atoms, similar to the sheets observed for the tetrameric form, $Ph_4Se_4Br_4$.

Introduction

Organoselenium halides have been known for many years and are versatile electrophilic reagents used in a range of different organic transformations.[1-3] Organoselenium halides are found in both the +2 (RSeX) and +4 ($RSeX_3$ / R_2SeX_2 / R_3SeX) oxidation states, and are usually synthesised via the reactions of halogens or halogenating agents with selenoethers or diselenides.[2]

The reactions of diselenides (R_2Se_2) with halogens produce both RSeX selenium(II) and $RSeX_3$ selenium(IV) species, depending on the ratio and oxidising power of the halogen, *e.g.* RSeF compounds are highly unstable with respect to disproportionation to $RSeF_3$ and R_2Se_2,[4] and reactions of R_2Se_2 with fluorinating agents such as XeF_2 usually result in the exclusive formation of $RSeF_3$ compounds.[4,5] Whilst both RSeX and $RSeX_3$ species can usually be formed when X = Cl and Br, there are no reports of $RSeI_3$ compounds. Reactions of R_2Se_2 with I_2 usually leads to products with an "RSeI" stoichiometry, although examples containing genuine covalent selenium–iodine bonds are rare.[6] The only examples known are with very bulky R groups such as 2,4,6–($^tBu)_3C_6H_2$,[7] 2,4,6–$(Me)_3C_6H_2$,[8] and C_6H_3–2,6–$[C_6H_3$–3,5–$\{2,6$–$(^iPr)_2C_6H_3\}_2]_2$ (Bpq).[9] The majority of ArSeI compounds (and many ArSeCl and ArSeBr compounds), are stabilised by short N···Se–I or O···Se–I intermolecular interactions from heteroatoms present on pendant arms on the aryl rings,[10] or by hypervalent coordination from non–bonded halide ions,[11] or halogen substituents on the aryl ring.[12] In this way a linear N/O/X···Se–X system is set up, which stabilises the Se–X bond. Recently, the structure of "MeSeI" was reported,[13] which exists in the solid–state as a CT compound, $Me_2Se_2I_2$, where the Se–Se bond is intact, and the I_2 molecule interacts with just one selenium atom. The same authors have also reported the structure of $Me_2Se_2.2I_2$ where I_2 molecules interact with both of the selenium atoms.[13]

The surprising structural diversity of RSeX compounds is illustrated by the "PhSeX" series (X = Cl, Br, I).[14-18] When X = Cl or Br tetrameric species, $Ph_4Se_4X_4$, are formed in the solid–state,[14,15] which consist of four PhSeX units linked together into a square by weak Se–Se bonds [2.993(3) to 3.051(2) Å], as shown in Fig. 1(a) for $Ph_4Se_4Br_4$. By contrast, PhSeI is a centrosymmetric dimer, $(Ph_2Se_2I_2)$[2,16] which is a CT species where one selenium atom acts as a donor towards iodine [Se–I: 2.992 Å], whilst the other behaves as a weak acceptor [Se–I: 3.588 Å].

There have been fewer structural studies reported for $RSeX_3$ systems. A small number of $RSeCl_3$ compounds have been structurally characterised and again show variations. The structure of $PhSeCl_3$ is polymeric, and consists of individual "saw–horse" shaped $PhSeCl_3$ units linked into a chain polymer by bridging chlorines, the overall geometry at selenium being square pyramidal, see Fig. 1(b).[19] Dimeric structures with two bridging chlorine atoms, $[RSeCl_2(\mu\text{–}Cl)_2RSeCl_2]$, have been established for CF_3SeCl_3,[20] 1,2–$(SeCl_3)_2C_6H_4$,[21] and 4–$(Me_3Si)_2N$–3,5–$(^iPr)_2C_6H_2SeCl_3$.[22] In the first two examples the R groups are on the same side of the Se_2Cl_6 unit (*cis* isomer), whilst in the latter the bulky substituted aryl rings are on opposite sides (*trans* isomer). The only other reported $RSeCl_3$ structure is $\{o\text{–}(Me_2NCH_2)C_6H_4\}SeCl_3$, where the selenium atom also bonds to the nitrogen atom on the pendant arm, resulting in a square pyramidal geometry. The monomeric units form a weak dimer linked by long Se···Cl interactions.[23]

The only reported structure of an $RSeBr_3$ compound is that of $PhSeBr_3$, which exhibits a very different structure from $PhSeCl_3$, see Fig. 1(c).[19] The geometry around the selenium atom is again square pyramidal, but the structure consists of a primary "$PhSeBr_2$" unit, with two additional weaker Se–Br bonds to bromide ions. These bromide ions (which are in a distorted tetrahedral environment) each interact with four different "$PhSeBr_2$" units. To complete the structure each of the two bromine atoms bound strongly to selenium (which are in a pyramidally distorted square planar environment) interact via Br···Br contacts to four "$PhSeBr_2$" units. The novel network structure of $PhSeBr_3$ is thus built up by extensive Se···Br and Br···Br contacts, and exhibits molecular, ionic and CT aspects.

Insert Fig. 1 near here

In view of the paucity of structural data reported for $RSeX_3$ systems, we decided to study the reactions of the *para*–substituted diaryl diselenides $(p\text{–}XC_6H_4)_2Se_2$ (X = F, Cl) with SO_2Cl_2 and Br_2. The compounds $(p\text{–}ClC_6H_4)SeCl_3$ and $(p\text{–}ClC_6H_4)SeBr_3$ are known,[24] but no structural details have emerged. The only solid–state investigation has been an IR / Raman spectroscopic study of $(p\text{–}ClC_6H_4)SeBr_3$ by Clark and Al–Turahi.[25] We now report a detailed structural and spectroscopic study of $(p\text{–}FC_6H_4)SeX_3$ (X = Cl, Br) and $(p\text{–}ClC_6H_4)SeX_3$ (X = Cl, Br).

Results and discussion

Synthesis of $ArSeX_3$ (X = Cl, Br) compounds

The $ArSeX_3$ (X = Cl, Br) compounds were prepared by the reaction of the diselenides $(p\text{–}FC_6H_4)_2Se_2$ and $(p\text{–}ClC_6H_4)_2Se_2$ with three molar equivalents of SO_2Cl_2, or Br_2, at ambient temperature in anhydrous diethyl ether. In the case of the trichlorides the products precipitated as cream coloured solids after several hours stirring. In contrast, the tribromides were considerably more soluble, and orange–red solids were isolated either by concentration (or complete removal) of the mother liquor to 10mL, followed by addition of pentane to precipitate the product. The compounds obtained were characterised by elemental analysis, multinuclear NMR spectroscopy, Raman spectroscopy and single crystal X–ray diffraction.

Structural studies of $(p\text{–}FC_6H_4)SeX_3$ (X = Cl, Br)

Crystals of $(p\text{–}FC_6H_4)SeCl_3$ were obtained directly from the reaction liquor (diethyl ether) on cooling, whilst crystals of $(p\text{–}FC_6H_4)SeBr_3$ were obtained from a chloroform solution of the compound layered with pentane. The structures of $(p\text{–}FC_6H_4)SeCl_3$ and $(p\text{–}FC_6H_4)SeBr_3$ are isomorphous (monoclinic, *C*2/*c*), and both exhibit a dimeric structure consisting of two $RSeX_3$ units of "saw–horse" geometry, linked together via two halide bridges, $RSeX_2(\mu\text{–}X)_2RSeX_2$. This type of dimeric structure differs considerably from the previously reported $PhSeX_3$ (X = Cl, Br) series, where the trichloride has a polymeric structure, and the tribromide forms a network structure.[19] These findings illustrate that the structure of $ArSeX_3$ (X = Cl, Br) compounds are dependent on the nature of the aryl group. A similar diversity in structure has been observed for $ArTeCl_3$ and $ArTeBr_3$ systems, where both $PhTeCl_3$ and $PhTeBr_3$ have chain polymeric structures,[26-27] but substituted aryl derivatives have been shown to exhibit other structural motifs. For example, $(p\text{–}OPhC_6H_4)TeCl_3$ is dimeric with *trans*–$(p\text{–}OPhC_6H_4)$ groups,[28] whilst a number of other $ArTeCl_3$ structures are polymeric but only have a single chloride bridge.[29-30] Other $ArTeBr_3$ structures usually have dimeric structures, such as $(p\text{–}EtOC_6H_4)TeBr_3$.[30]

The molecular structures of $(p\text{–}FC_6H_4)SeCl_3$ and $(p\text{–}FC_6H_4)SeBr_3$ are shown in Figs. 2 and 3 respectively, along with selected bond lengths and angles. As a result of dimerisation, the selenium atoms in both $(p\text{-}FC_6H_4)SeCl_3$ and $(p\text{–}FC_6H_4)SeBr_3$ are in a square pyramidal geometry, with two terminal and two bridging halogen atoms, and the $p\text{-}FC_6H_4$ rings in the apical position. The $p\text{-}FC_6H_4$ rings bound to each of the selenium atoms are located on the same side of the Se_2X_6 plane, therefore both structures exhibit a *cis*–configuration. The essentially co–planar arrangement of all the selenium and halogen atoms in the both structures contrasts with the previously reported *cis*–dimeric structure of CF_3SeCl_3, which is a folded dimer where each selenium atom is co–planar to the four chlorine atoms bound to it, but is not co–planar to the second selenium atom and two terminal chlorine atoms at the other side of the dimer.[20] This folding is likely to be due to a steric clash between the two bulky CF_3 groups. In the structure of $(p\text{-}FC_6H_4)SeCl_3$, the two $p\text{-}FC_6H_4$ rings bend slightly towards one another and stack directly over each other with a C(*ipso*)–Se···Se–C(*ipso*) torsion angle of 0.0°. The structure of $(p\text{-}FC_6H_4)SeBr_3$ also shows the two aryl rings bending towards each other, although here the rings are slightly offset, with a C(*ipso*)–Se···Se–C(*ipso*) torsion angle of 3.44°.

Insert Figs. 2 and 3 near here

In both structures the bridging Se–X bonds are significantly longer than the terminal Se–X bonds, and there is asymmetry in both the magnitude of the bridging Se–X bonds, and of the terminal Se–X bonds. This results in the shorter terminal Se–X bond being *trans* to the longer bridging Se–X bond, and *vice versa*. This type of *trans*–effect has long been established for main group halogen compounds,[31,32] and is particularly pronounced for bridged systems where a lone pair is present, as is the case for selenium(IV) halide species. The structures are thus closely related to anionic systems such as $[Se_2X_{10}]^{2-}$ (X = Cl, Br).[32,33] The overall distances across the four linear X–Se–X angles in each of the (p-FC_6H_4)SeX_3 structures are fairly consistent, 4.83 to 4.97 Å in (p-FC_6H_4)$SeCl_3$, and 5.17 to 5.27 Å in (p–FC_6H_4)$SeBr_3$. Without the *trans*–effect this would result in an average Se–Cl bond of 2.41 to 2.48 Å, and an average Se–Br bond of 2.58 to 2.63 Å. The terminal Se–X bonds (see Figs. 2 and 3 and Table 1) are similar to the sum of the covalent radii for the relevant elements (Se & Cl: 2.15 to 2.22 Å, Se & Br: 2.30 to 2.40 Å),[34-35] with considerably longer bridging Se–X bonds. The bonding at selenium can be interpreted as containing two orthogonal three–centered four–electron (3c–4e) X–Se–X fragments crossing at selenium, with a more conventional 2c–2e bond to the aryl ring. The 3c–4e systems result in X–Se–X angles which are somewhat deviated from linear, due to the asymmetry in the Se–X bonds. The *trans* X–Se–X angles in (p-FC_6H_4)$SeCl_3$ vary between 172.15(9)° and 175.29(9)°, and those in (p–FC_6H_4)$SeBr_3$ between 169.33(9)° and 173.09(8)°.

Insert Table 1 near here

The structures of (p-FC_6H_4)$SeCl_3$ and (p–FC_6H_4)$SeBr_3$ have been compared with the small number of previously reported $RSeCl_3$ and $RSeBr_3$ structures, and with examples of the related $[Se_2X_{10}]^{2-}$ (X = Cl, Br) anions,[33,36-40] see Table 1. The magnitude of the terminal and bridging Se–Cl bonds in (p-FC_6H_4)$SeCl_3$ are consistent with those observed for other dimeric $RSeCl_3$ species and $[Se_2Cl_{10}]^{2-}$ anions, though the latter show a wider spread for the bridging Se–Cl bonds.

Similarly, the structure of (p–FC_6H_4)$SeBr_3$ displays terminal Se–Br bonds comparable in length to those in $PhSeBr_3$ despite the very different structures. However, the additional secondary Se···Br interactions in $PhSeBr_3$ are considerably longer than the bridging Se–Br bonds in (p–FC_6H_4)$SeBr_3$, and those in $[Se_2Br_{10}]^{2-}$ anions.

The structures of (p-FC_6H_4)$SeCl_3$ and (p–FC_6H_4)$SeBr_3$ both exhibit a secondary Se···X interaction to the vacant sixth coordination site, resulting in a weak pairing of dimers, as shown for (p-FC_6H_4)$SeCl_3$ in Fig. 4. This expansion of the coordination environment to six is a common feature of organo–selenium(IV) halide structures, such as CF_3SeCl_3,[20] and Me_2SeX_2 (X = Cl, Br).[41] However, it should be noted that no secondary Se···Cl interactions were observed for 4–$(Me_3Si)_2N$–3,5–$(^iPr)_2C_6H_2SeCl_3$, (planar dimer with *trans* aryl groups), presumably due to the high steric bulk of the aryl groups.[22] Both of the (p-FC_6H_4)SeX_3 structures display two secondary Se···X interactions, Se(1)···Cl(4): 3.390(2) Å / Se(2)···Cl(3): 3.402(3) Å in (p-FC_6H_4)$SeCl_3$, and Se(2)···Br(6): 3.506(15) Å / Se(1)···Br(3): 3.549(2) Å in (p–FC_6H_4)$SeBr_3$. These distances are considerably longer than the primary Se–X bonds in the dimers, but are still significantly shorter than the sum of the relevant van der Waals radii (for Se & Cl: 3.65 Å, Se & Br: 3.73 Å).[42] In each of the two structures pairs of dimers stack diagonally down the cell parallel to the *c*–axis. In (p-FC_6H_4)$SeCl_3$ these pairs are linked by a weak non–classical hydrogen bond, Cl(2)···H(8) of 2.91 Å , see Fig. 4, whilst in (p–FC_6H_4)$SeBr_3$ the most significant contacts between pairs are weak Br···Br contacts of 3.541(2) Å. The extended structures are shown in the supplementary data, and feature extensive π–stacking of the p–FC_6H_4 rings, and aggregation of the fluorine atoms into fluorophillic regions.

Insert Fig. 4 near here

Structural studies of (p–ClC_6H_4)SeX_3 (X = Cl, Br)

Small crystals of (p–ClC_6H_4)$SeCl_3$ were obtained by warming an acetonitrile solution of the compound, followed by refrigeration for two weeks. Crystals of (p–ClC_6H_4)$SeBr_3$ were obtained from a dichloromethane solution of the compound layered with diethyl ether. In contrast to the (p-FC_6H_4)SeX_3 (X = Cl, Br) series the two compounds are not directly isostructural. The structure of (p–ClC_6H_4)$SeCl_3$ (monoclinic, *C*2/*c*) contains two independent molecules in the asymmetric unit. Both of these molecules are dimeric but whilst one dimer exhibits a *cis*–arrangement of the (p-ClC_6H_4) rings, the other has a *trans*– arrangement, with the aryl rings on opposite sides of the Se_2Cl_6 plane. Other $ArEX_3$ structures are known where both the *cis*– and *trans*–isomers can be crystallised, such as $PhTeI_3$,[43] but to the best of our knowledge this is the first example where both isomers are co–crystallised in the same unit cell. The molecular structure of (p–ClC_6H_4)$SeCl_3$ is shown in Fig. 5, along with selected bond lengths and angles.

Insert Fig. 5 near here

All the selenium and chlorine atoms are co–planar in both the *cis*– and *trans*–dimers, with the (p–ClC_6H_4) rings again occupying the apical position of the square pyramid at each selenium atom. The increase in steric bulk upon going from (p–FC_6H_4) to (p–ClC_6H_4) means that the two rings do not directly overlap as was the case for (p-FC_6H_4)$SeCl_3$, and the C(*ipso*)–Se···Se–C(*ipso*) torsion angle for the *cis*–dimer of (p–ClC_6H_4)$SeCl_3$ is 5.60°. The same torsion angle for the *trans*–dimer is 180.0°, due to the presence of a crystallographic inversion centre which was also previously observed for the *trans*–dimeric structure of 4–$(Me_3Si)_2N$–3,5–$(^iPr)_2C_6H_2SeCl_3$.[22]

The magnitude of the Se–Cl bonds in the structure can be compared to (p-FC_6H_4)$SeCl_3$ and other $RSeCl_3$ structures, see Table 1. The *trans* effect of the Se–Cl bonds is apparent in both dimers, but whilst the asymmetry of the terminal Se–Cl bonds is similar in each of the dimers, the asymmetry of the bridging Se–Cl bonds is significantly more pronounced in the *trans*–dimer than in the *cis*. The result is that whilst the overall linear Cl–Se–Cl distance is fairly consistent in the *cis*–dimer (between 4.86 and 4.94 Å), in the *trans*–dimer there is a wider disparity (4.85 and 5.01 Å), and the *trans* form is thus more loosely linked into dimers than the *cis*. A comparison of the angles around the selenium atoms in both structures shows that they are close to the expected angles for a square–based pyramidal geometry. The *trans*–dimer of (p-ClC_6H_4)$SeCl_3$ shows a more distorted geometry at selenium than the *cis*–dimer, with the linear Cl–Se–Cl angles varying between 167.94(7)° and 172.31(8)°, compared with 172.30(7)° and 176.72(7)° in the *cis*–dimer.

In the extended structure of (p-ClC$_6$H$_4$)SeCl$_3$ the presence of a secondary Se···Cl contact to extend the geometry at selenium to six is not consistently observed. The Se(1) atom in the *cis*–dimer exhibits an interaction to one of the bridging chlorine atoms of the *trans*–dimer, Se(1)···Cl(11): 3.3542(19) Å, but no such secondary Se···Cl contacts are observed either at the other selenium atom in the *cis*–dimer, or the selenium atoms of the *trans*–dimer. Both *cis*– and *trans*–dimers stack down the crystallographic *b*–axis, with extensive π–stacking of the *p*–ClC$_6$H$_4$ rings, as shown in Fig. 6. The crystal packing also features a number of Cl···Cl interactions which act in concert with the Se···Cl interactions to link the dimeric units, see supplementary data.

Insert Fig. 6 near here

Crystals of (p–ClC$_6$H$_4$)SeBr$_3$ were solved in the monoclinic space group $P2_1/n$. The compound has a *cis*–dimeric structure, but in contrast to (p–FC$_6$H$_4$)SeBr$_3$ it is a folded dimer rather than planar. The molecular structure of (p–ClC$_6$H$_4$)SeBr$_3$ is shown in Fig. 7 along with selected bond lengths and angles.

Insert Fig. 7 near here

The dimeric structure of (p–ClC$_6$H$_4$)SeBr$_3$ is considerably more bent at the bridging bromine atoms than (p–FC$_6$H$_4$)SeBr$_3$, leading to a highly folded dimeric structure. The Se–Br–Se angles at the bridging bromine atoms are 80.52(4)° and 81.44(4)°, compared to 94.27(6)° and 96.87(6)° in the planar dimer of (p–FC$_6$H$_4$)SeBr$_3$. The magnitude of the terminal Se–Br bonds in (p–ClC$_6$H$_4$)SeBr$_3$ are consistent with those observed for (p–FC$_6$H$_4$)SeBr$_3$, whereas the bridging Se–Br bonds cover a much wider range, see Table 1. The much greater asymmetry in the bridging Se–Br bonds compared with those in (p–FC$_6$H$_4$)SeBr$_3$ is likely to be a consequence of the folded nature of the dimer. This increase in asymmetry also results in a small increase in distortion of the angles around selenium. The linear Br–Se–Br angles around the selenium atoms vary between 166.32(5)° and 170.45(6)°, compared to values of 169.33(9)° to 173.09(8)° for (p–FC$_6$H$_4$)SeBr$_3$.

The extended structure again shows secondary Se···Br interactions to the vacant sixth coordination site on both selenium atoms which results in pairing of dimers. However, in contrast to (p–FC$_6$H$_4$)SeBr$_3$ both selenium atoms interact with the same bromine atom of a neighbouring dimer, Se(1)···Br(3): 3.4107(14) Å and Se(2)···Br(3): 3.3976(14) Å, as shown in Fig. 8. This change in the "pairing motif" is likely to be due to the folded nature of the dimer, although it allows closer approach of pairing dimers, as the secondary interactions are shorter than those of 3.506(15) and 3.549(2) Å observed for the planar dimer (p–FC$_6$H$_4$)SeBr$_3$.

Insert Fig. 8 near here

Each of these "paired" dimers then stack down the *a*–cell dimension linked to neighbouring pairs by long Br···Br contacts, Br(1)···Br(5): 3.5329(15) Å and Br(2)···Br(6): 3.5536(16) Å. The extended structure again features extensive π–stacking, and is discussed in more detail in the supplementary information.

Raman spectroscopic studies

The Raman spectrum of (p–FC$_6$H$_4$)SeCl$_3$ displays three strong bands between 368 and 303 cm^{-1} and five weaker intensity bands between 272 and 168 cm^{-1}, whilst the spectrum of (p–ClC$_6$H$_4$)SeCl$_3$ displays two strong bands between 357 and 307 cm^{-1} and five weaker bands between 249 and 118 cm^{-1}. The intense peaks above 300 cm^{-1} are likely to be due to ν(Se–Cl) stretching bands, by comparison with the data observed for PhSeCl$_3$.[19] The weaker intensity bands may be due to a combination of ν(Se–Ph) modes, bridging ν(Se–Cl) bands, or Se–Cl bending modes.

Clark and Al–Turahi have previously reported far IR and Raman spectroscopic data for a series of ArSeBr$_3$ compounds, including (p–ClC$_6$H$_4$)SeBr$_3$.[25] They concluded that the spectra were consistent with a distorted octahedral environment with approximate C_{3v} symmetry, where there are three short bonds (two Se–Br and one Se–C) and three long (Se–Br) bonds, and therefore interpreted the structure as ionic, consisting of [ArSeBr$_2$]$^+$ cations and [Br]$^-$ anions, and probably linked into a tetramer, as in the related structure of SeBr$_4$.[44] However, this interpretation also fits the ArSeBr$_3$ dimeric structures reported herein for (p–XC$_6$H$_4$)SeBr$_3$ (X = F, Cl), when considering the nature of the bonds, as previously discussed. We observe four strong bands between 260 and 187 cm^{-1} for (p–FC$_6$H$_4$)SeBr$_3$ and three bands between between 271 and 182 cm^{-1} for (p–ClC$_6$H$_4$)SeBr$_3$ which are assigned as ν(Se–Br) stretching bands.

NMR spectroscopic studies of the ArSeX$_3$ (X = Cl, Br) compounds

The ^{1}H, ^{13}C{^{1}H} and ^{77}Se{^{1}H} NMR spectra of (p–XC$_6$H$_4$)SeCl$_3$ and (p–XC$_6$H$_4$)SeBr$_3$ (X = F, Cl) were recorded in CDCl$_3$ solution, with the anticipated peaks of the substituted aryl rings being observed in the ^{1}H and ^{13}C{^{1}H} NMR spectra. The ^{77}Se{^{1}H} NMR spectra of the ArSeCl$_3$ compounds display singlet resonances at 618 ppm for (p–FC$_6$H$_4$)SeCl$_3$ and 622 ppm for (p–ClC$_6$H$_4$)SeCl$_3$. To the best of our knowledge the only reported ^{77}Se{^{1}H} NMR data for an RSeCl$_3$ compound is for 4–(Me$_3$Si)$_2$N–3,5–(^{i}Pr)$_2$C$_6$H$_2$SeCl$_3$, (δ$_{Se}$: 940 ppm).[22] The significantly lower frequencies observed here suggest that the nature of the aryl group has a significant impact of the ^{77}Se chemical shift. This dependency on the R group has also been observed for related ArSeCl species, which commonly display δ$_{Se}$ between 900 and 1050 ppm,[45-48] for example δ$_{Se}$: 1045 ppm for PhSeCl,[15] although the shift for the fully fluorinated (C$_6$F$_5$)SeCl is observed at 801 ppm.[46] The NMR data is suggestive that the ArSeCl$_3$ species reported here are monomeric in solution (with saw–horse geometry at selenium), as only a single peak was observed for (p–ClC$_6$H$_4$)SeCl$_3$ rather than two, which would be expected if both *cis*– and *trans*–dimeric forms were retained in solution.

In contrast, the ^{77}Se{^{1}H} NMR spectra of the (p–XC$_6$H$_4$)SeBr$_3$ compounds exhibit peaks at 857 ppm (X = F), and 847 ppm (X =

Cl). Whilst there is no reported $^{77}Se\{^1H\}$ NMR data for $RSeBr_3$ species, the peaks observed here for the (p–XC_6H_4)$SeBr_3$ compounds are close to the shift reported (δ_{Se}: 867) for the selenium(II) species PhSeBr.[14] Wynne and Pearson have previously reported that $PhSeBr_3$ is approx. 80% dissociated in solution to PhSeBr and Br_2, based on cryoscopic molecular weight measurements.[49] We therefore recorded the $^{77}Se\{^1H\}$ NMR spectrum of a sample of $PhSeBr_3$ in $CDCl_3$, which displayed only one peak at 861 ppm, which is close to the literature value for PhSeBr,[14] and therefore agrees with the observations of Wynne and Pearson. Indeed, the dissociation of selenium(IV) bromide species such as $SeBr_4$ and Ph_2SeBr_2 has been long known,[50-52] with the order of degree of dissociation being $SeBr_4 > PhSeBr_3 > Ph_2Se_2Br_2$.[49,50]

It therefore appears from the solution–phase NMR spectroscopic data that both (p–FC_6H_4)$SeBr_3$ and (p–ClC_6H_4)$SeBr_3$ exhibit similar behaviour to $PhSeBr_3$, and both dissociate in $CDCl_3$ to give "ArSeBr" species and Br_2, in contrast to the (p–XC_6H_4)$SeCl_3$ (X = F, Cl) compounds which do not appear to dissociate in solution.

Crystal structure of $Ph_2Se_2Br_2$

In view of the similar solution phase behaviour of the two (p–XC_6H_4)$SeBr_3$ compounds and $PhSeBr_3$ we decided to investigate whether a dimeric form of $PhSeBr_3$ could also be obtained by varying the re–crystallisation solvent. The previously reported network structure of $PhSeBr_3$ was obtained from cooling of a warmed diethyl ether solution of the compound.[19] We recrystallised a sample of $PhSeBr_3$ (from dichloromethane layered with diethyl ether), resulting in the formation of a mixture of dark orange and pinkish purple crystals. An examination of the unit cell of the orange crystals showed that they were the previously reported $PhSeBr_3$. However, the purple crystals were crystallographically characterised and shown to be a selenium(II) species, $Ph_2Se_2Br_2$, which consists of two "PhSeBr" units linked together by a Se–Se bond. This structure contrasts with the established structure of the commercially available "PhSeBr" reagent which forms deep purple crystals of the tetrameric $Ph_4Se_4Br_4$ compound, which consists of four "PhSeBr" units linked into a square motif by weak Se···Se interactions.[14] The structure of $Ph_2Se_2Br_2$ is shown in Fig. 9, along with selected bond lengths and angles.

Insert Fig. 9 near here

$Ph_2Se_2Br_2$ crystallises in the monoclinic space group $P2_1$ and contains an elongated Se–Se bond of 2.832(4) Å which links two PhSeBr fragments. This Se–Se bond is considerably longer than that of diphenyl diselenide, 2.29(1) Å,[53] but significantly shorter than the very weak Se–Se bonds in the tetrameric form ($Ph_4Se_4Br_4$), where the distances vary between 3.004(2) and 3.051(2) Å.[14] The structure of $Ph_2Se_2Br_2$ is reminiscent of half of the structure of $(Ph_2Se_2I_2)_2$, which is a CT dimer.[16] The Se–Se bond in $(Ph_2Se_2I_2)_2$ is much shorter (2.347 Å) than the Se–Se bond in $Ph_2Se_2Br_2$, which reflects the nature of $(Ph_2Se_2I_2)_2$ where the Ph_2Se_2 group is much less perturbed and dimerises via weaker CT interactions.[16] The structure of $Ph_2Se_2Br_2$ contrasts with that of "PhTeBr" which although also exhibiting a structure of formula $Ph_2E_2Br_2$ (with an intact E–E bond), has a very different structure, where bromine has added across only one of the two tellurium atoms, resulting in one oxidised tellurium atom in a "saw–horse" geometry, and one unoxidised tellurium atom in a bent geometry.[54]

There is considerable variation in the two Se–Br bonds in $Ph_2Se_2Br_2$, where the Se(1)–Br(1) bond is 2.449(4) Å, and the Se(2)–Br(2) bond is 2.352(5) Å. The Se–Br bonds in $Ph_4Se_4Br_4$ are intermediate between these values, ranging between 2.381(2) and 2.391(2) Å.[14] The elongated Se(1)–Br(1) bond may be considered to be a bridging Se–Br bond, as atom Br(1) weakly bridges to the Se(2) atom of a neighbouring $Ph_2Se_2Br_2$ molecule, see Fig. 10. This Br(1)···Se(2) contact of 3.333(4) Å is much longer than either of the two Se–Br bonds, but is well within the sum of the van der Waals radii of Se and Br, 3.73 Å.[42]

Insert Fig. 10 near here

The structure thus propagates in a chain polymeric fashion, with atom Se(1) in a T–shaped geometry, and atom Se(2) in a "saw–horse" geometry as a result of the additional contact. The structure further extends by very weak contacts from the "terminal" Br(2) atom to both atoms Br(1) and Se(1) of a neighbouring chain, Se(1)···Br(2): 3.691(5) Å, and Br(1)···Br(2): 3.665(4) Å. A sheet of selenium and bromine atoms is therefore formed which is similar to that observed for $Ph_4Se_4Br_4$,[14] where the extended solid–state structure consists of planar sheets made up of Se_4 and Br_4 squares, with the phenyl rings stacking between the sheets. The sheet of selenium and bromine atoms in $Ph_2Se_2Br_2$ is more rippled, but still essentially planar, and is made up of 5–membered Se_2Br_3 rings, and 7–membered Se_3Br_4 rings, see Fig. 11. The phenyl rings then stack between the sheets, see Fig 12.

Insert Fig. 11 and 12 near here

Conclusions

The series of (p–XC_6H_4)$SeCl_3$ and (p–XC_6H_4)$SeBr_3$ compounds (X = F, Cl) exhibit doubly bridged $ArSeX_2(\mu\text{–}X)_2ArSeX_2$ dimeric structures, in contrast to $PhSeCl_3$ (chain polymer) and $PhSeBr_3$ (network structure). (p–FC_6H_4)$SeCl_3$ and (p–FC_6H_4)$SeBr_3$ are planar dimers with the aryl rings on the same side of the plane (*cis*–dimers), whilst (p–ClC_6H_4)$SeCl_3$ co–crystallises as a mixture of *cis*– and *trans*–planar dimers, and (p–ClC_6H_4)$SeBr_3$ adopts a folded *cis*–dimeric structure. These dimers feature the selenium atom in a square pyramidal geometry with an additional weak Se···X interaction usually observed at the vacant sixth coordination site. The exception is in the structure of (p–ClC_6H_4)$SeCl_3$ where only one of the selenium atoms in the *cis*–dimer has a secondary Se···Cl interaction, with no such interactions observed in the *trans*–dimer.

An NMR spectroscopic study of the $ArSeX_3$ species suggests that in solution the $ArSeCl_3$ compounds exist as monomers, whilst the $ArSeBr_3$ compounds extensively dissociate to ArSeBr and Br_2.

A second structural isomer of "PhSeBr" has been crystallographically characterised. In contrast to the previously reported "$Ph_4Se_4Br_4$" form, $Ph_2Se_2Br_2$ exists as a dimer with an elongated Se–Se bond of 2.832(4) Å. This form of "PhSeBr" was isolated as crystals from a solution of $PhSeBr_3$, where dissociation to PhSeBr and Br_2 had occurred. The extended structure forms a chain polymer via linking of $Ph_2Se_2Br_2$ molecules by Se···Br interactions, and then further into sheets of selenium and bromine atoms by weaker Se···Br and Br···Br interactions. The isolation of a second structural form of "PhSeBr" may be a consequence of this form being obtained via dissociation of $PhSeBr_3$ in solution.

The structures reported herein further illustrate the wide structural diversity of ArSeX and $ArSeX_3$ species, where small changes in the nature of either the aryl group or the halide may result in the formation of different structural motifs.

Experimental

Reagents and physical measurements

The compounds synthesised herein are sensitive to moisture, therefore standard Schlenk techniques were employed throughout, with all additions being performed in an argon–filled glove box. Diethyl ether was purchased commercially (BDH) and freshly distilled from sodium/benzophenone ketyl before use. Deuterated chloroform (Goss Scientific, dried over molecular sieves) was obtained commercially. $(p\text{–}FC_6H_4)_2Se_2$ was prepared via a modification of the literature method of Pappalardo and co–workers,[55] as outlined below. $(p\text{–}ClC_6H_4)_2Se_2$, magnesium turnings, selenium powder, sulfuryl chloride and bromine were all purchased commercially (Aldrich), whilst 1–bromo–4–fluorobenzene was purchased from Fluorochem. All reagents were used as received. Elemental analyses were performed by the University of Manchester Departmental Microanalytical service. Raman spectra were collected as solid samples on a Nicolet–Nexus combined FT–IR/FT–Raman spectrometer, using the OMNIC E.S.P 5.1 software package. Spectra were recorded to the low frequency cut–off point of 100 cm^{-1}. ^1H, $^{13}C\{^1H\}$, and $^{77}Se\{^1H\}$ NMR spectra were recorded on a Bruker AVANCE III 400 spectrometer operating at 400.1, 100.6 and 76.3 MHz respectively. Peak positions are quoted relative to external TMS ($^1H/^{13}C$) or Me_2Se (^{77}Se), using the high frequency positive convention throughout.

Crystallographic details

Details of the structural analyses are summarised in Table 2. Diffraction data were recorded on a Nonius κ–CCD four–circle diffractometer using graphite–monochromated Mo–Kα radiation (λ = 0.71073 Å), at 100(2) K. Structural data were solved by direct methods, with full–matrix least squares refinement on F^2 using the SHELX–97 program.[56] Absorption corrections were applied by the multi–scan method using the SORTAV program.[57] Non–hydrogen atoms were refined with anisotropic thermal parameters, whilst all hydrogen atoms were modelled in ideal positions. Flack parameter for $Ph_2Se_2Br_2$ is 0.18(14). All thermal ellipsoid plots were generated using ORTEP–3 for Windows,[58] and other pictures generated using the MERCURY program.[59] Crystallographic data has been deposited at the CCDC, reference numbers XXX–XXX. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Insert Table 2 near here

Synthetic details

Synthesis of $(p\text{–}FC_6H_4)_2Se_2$: 3.159 g of magnesium turnings (0.130 moles) were added under a stream of dry nitrogen to a three necked round bottomed flask containing 250 mL of sodium–dried diethyl ether. 20.0 g (12.55 mL, 0.114 moles) of 1–bromo–4–fluorobenzene in 100 mL of dry ether was added dropwise by means of a pressure equalizing dropping funnel. The rate of addition was controlled so as to maintain a gentle reflux of the solution (initiation of the Grignard with a drop of 1,2–dibromoethane may be necessary). Once all of the 1–bromo–4–fluorobenzene was added the solution was left to stir at room temperature until all of the magnesium turnings had been consumed (around one hour). After this time 9.79 g (0.124 moles) of selenium powder was added to the solution in approx. 0.5 g portions over the course of 30 minutes. The olive–green solution was then stirred at ambient temperature for two hours. The system was then left stirring overnight with a stream of air bubbling through the solution. The product was extracted by shaking with 3 x 50 mL portions of 3.0 M dilute HCl (CAUTION: exothermic), followed by separation of the diethyl ether phase. The organic phase was dried over magnesium sulfate, filtered, and the solvent removed in vacuo to yield analytically pure $(p\text{–}FC_6H_4)_2Se_2$ in the form of an orange oil (16.35 g, 82.2% yield). Characterising data: Calculated for $C_{12}H_8F_2Se_2$: C, 41.4; H, 2.3; Found: C, 41.6; H, 2.5%. ^1H NMR ($CDCl_3$): 6.92–7.08 [m, 4H], 7.44–7.68 [m, 4H]. $^{13}C\{^1H\}$ NMR ($CDCl_3$): 116.4 [d, C_m, $^2J(CF) = 21.2$], 125.7 [s, C_i], 134.8 [d, C_o, $^3J(CF) = 8.2$], 163.0 [d, C_p, $^1J(CF) = 248.3$]. ^{19}F NMR ($CDCl_3$): 112.8 [s, br]. $^{77}Se\{^1H\}$ NMR ($CDCl_3$): 491.4 [s].

Synthesis of $ArSeX_3$ (X = Cl, Br) adducts

$(p\text{–}FC_6H_4)SeCl_3$: 0.740 g (2.1 x 10^{-3} moles) of $(p\text{–}FC_6H_4)_2Se_2$ was dissolved in 30 mL of anhydrous Et_2O. Under a stream of dry nitrogen 0.52 mL (0.861 g / 6.4 x 10^{-3} moles) of SO_2Cl_2 was added dropwise. The yellow solution turns an orange–brown colour, with gradual precipitation of a yellowish solid over two hours. The reaction was left to stir for *ca.* 5 days, after which time the solid was isolated using standard Schlenk techniques, and dried *in vacuo* to yield the product as a cream coloured solid in 71.5 % yield. Calculated for $C_6H_4FCl_3Se$: C, 25.7; H, 1.4; Cl, 38.0; Found: C, 25.9; H, 1.5; Cl, 37.7%. ^1H NMR ($CDCl_3$): 6.92–7.18 [m, 2H], 7.66–7.78 [m, 2H]. $^{13}C\{^1H\}$ NMR ($CDCl_3$): 117.0 [d, C_m, $^2J(CF) = 22.2$], 133.1 [s, C_i], 138.1 [s, C_o], 164.3 [d, C_p, $^1J(CF) = 253.6$]. $^{77}Se\{^1H\}$ NMR ($CDCl_3$): 618 [s]. Raman: 3072, 1583, 1483, 1294, 1232, 1163, 1039, 1005, 808, 731, 688, 627, 368, 345, 303, 272, 249, 206, 187, 168.

(p–ClC_6H_4)$SeCl_3$: Was synthesised as (p–FC_6H_4)$SeCl_3$ above except using 0.632 g (1.7 x 10^{-3} moles) of (p–ClC_6H_4)$_2Se_2$ and 0.40 mL (0.671 g / 5.0 x 10^{-3} moles) of SO_2Cl_2 in anhydrous Et_2O. The product was formed as a cream coloured solid in 66.2 % yield. Mpt. 175–179°C (172°C lit.)[24] Calculated for $C_6H_4Cl_4Se$: C, 24.2; H, 1.3; Cl, 47.8; Found: C, 24.4; H, 1.3; Cl, 47.6%. ^1H NMR ($CDCl_3$): 7.20 [s, 2H, ^3J(HH) = 8.4 Hz], 7.54 [s, 2H, ^3J(HH) = 8.4 Hz]. $^{13}C\{^1H\}$ NMR ($CDCl_3$): 124.8 [s, C_i], 129.8 [s, C_m], 135.8 [s, C_o], 137.0 [s, C_p]. $^{77}Se\{^1H\}$ NMR ($CDCl_3$): 622 [s]. Raman: 3114, 3056, 1564, 1180, 1094, 1036, 993, 722, 623, 357, 307, 249, 199m, 174, 137, 118.

(p–FC_6H_4)$SeBr_3$: 0.585 g (1.7 x 10^{-3} moles) of (p–FC_6H_4)$_2Se_2$ was dissolved in 30 mL of anhydrous Et_2O. Under a stream of argon 0.260 mL (0.809 g / 5.0 x 10^{-3} moles) of Br_2 was added dropwise. The deep orange–red solution was left to stir for *ca*. 12 hours, after which time the solvent was removed *in vacuo* to leave a sticky orange solid. The residue was washed with 2 x 5 mL of anhydrous pentane and dried for two hours to leave an orange solid (53.6 % yield). Calculated for $C_6H_4FBr_3Se$: C, 17.4; H, 1.0; Br, 58.0; Found: C, 17.2; H, 1.1; Br, 58.2%. ^1H NMR ($CDCl_3$): 6.93–7.01 [m, 2H], 7.72–7.77 [m, 2H]. $^{13}C\{^1H\}$ NMR ($CDCl_3$): 116.9 [d, C_m, ^2J(CF) = 21.2], 124.2 [s, C_i], 138.5 [d, C_o, ^3J(CF) = 9.2], 164.3 [d, C_p, ^1J(CF) = 252.6]. $^{77}Se\{^1H\}$ NMR ($CDCl_3$): 857 [s]. Raman: 3064, 1583, 1479, 1398, 1298, 1236, 1163, 1063, 1039, 1005, 808, 627, 337, 260, 245, 202, 187.

(p–ClC_6H_4)$SeBr_3$: Was synthesised as (p–FC_6H_4)$SeBr_3$ above, except using 0.635 g (1.7 x 10^{-3} moles) of (p–ClC_6H_4)$_2Se_2$ and 0.256 mL (0.799 g / 5.0 x 10^{-3} moles) of Br_2 in anhydrous Et_2O. The deep orange–red solution was left to stir for *ca*. 12 hours, concentrated in volume to *ca*. 5 mL, and 10 mL of anhydrous pentane was added. The product precipitated as an orange–red solid (49.4 % yield). Mpt. 120–123°C (123–124°C lit.)[24] Calculated for $C_6H_4ClBr_3Se$: C, 16.7; H, 0.9; Cl, 8.2; Br, 55.7; Found: C, 16.9; H, 0.8; Cl, 7.9; Br, 55.8%. ^1H NMR ($CDCl_3$): 7.28 [s, 2H, ^3J(HH) = 8.5 Hz], 7.69 [s, 2H, ^3J(HH) = 8.5 Hz]. $^{13}C\{^1H\}$ NMR ($CDCl_3$): 127.4 [s, C_i], 129.8 [s, C_m], 136.5 [s, C_o], 137.1 [s, C_p]. $^{77}Se\{^1H\}$ NMR ($CDCl_3$): 847 [s]. Raman: 3118, 3060, 1556, 1182, 1094, 1040, 990, 719, 623, 345, 310, 271, 209, 182, 154, 112.

Formation of dimeric form of "PhSeBr": $Ph_2Se_2Br_2$

A sample (*ca*. 0.20 g) of $PhSeBr_3$ (formed via the method outlined previously),[19] was dissolved in 10 mL of dry dichloromethane in a rotaflo tube, and 20 mL of dry diethyl ether was carefully syringed on top to form two separate layers. The tube was sealed and the layers allowed to slowly mix. A mixture of orange crystals ($PhSeBr_3$) and pink–purple crystals ($Ph_2Se_2Br_2$) were formed. A sample of the crystals of $Ph_2Se_2Br_2$ were removed from the tube and characterised. Calculated for $C_{12}H_{10}Br_2Se_2$: C, 30.5; H, 2.1; Br, 33.9; Found: C, 30.9; H, 2.2; Br, 33.8%. ^1H NMR ($CDCl_3$): 7.32–7.44 [m, 3H], 7.70–7.86 [m, 2H].

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‡ This paper is dedicated to the memory of Dr Steve Godfrey (1966-2011).

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Figures, Tables and captions

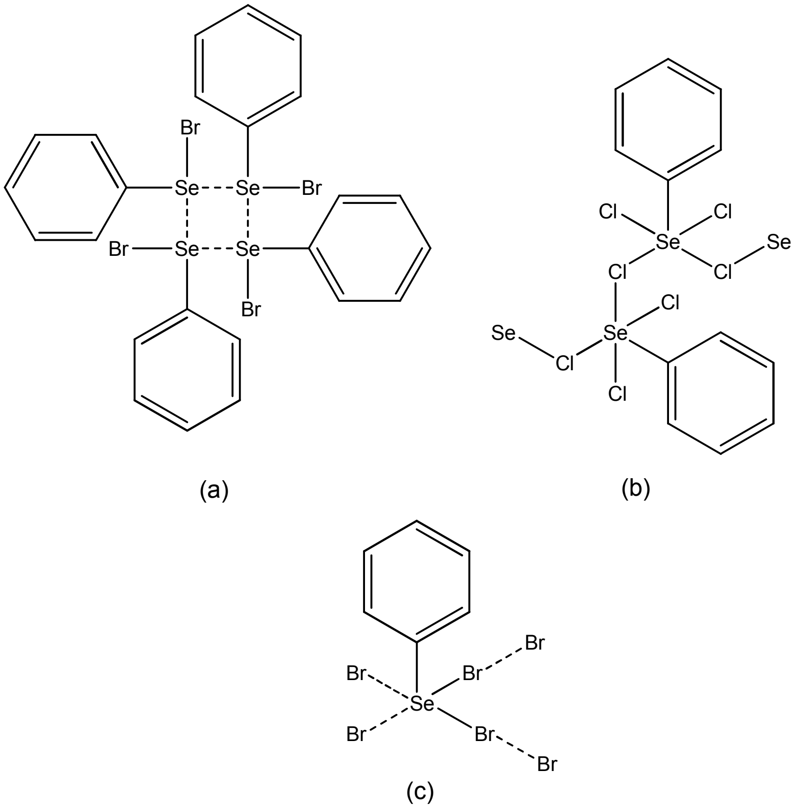

Figure 1 (a) Structure of $Ph_4Se_4Br_4$ showing “square” motif, (b) Part of the polymeric chain structure of $PhSeCl_3$, (c) Repeat unit of the network structure of $PhSeBr_3$.

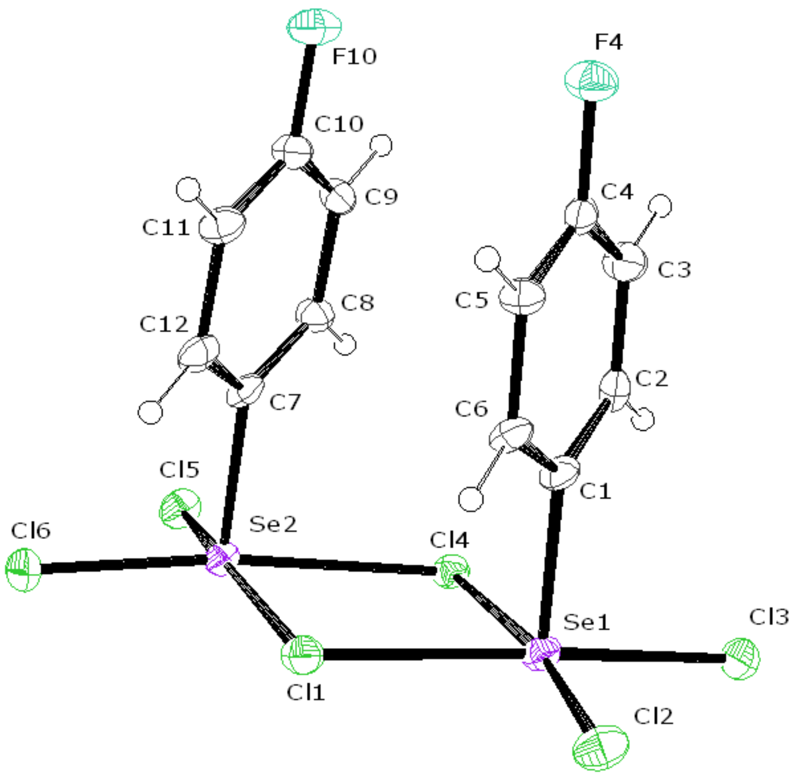

Figure 2 ORTEP representation of the molecular structure of (*p*-FC_6H_4)$SeCl_3$. Thermal ellipsoids are shown at the 30% probability level. Selected bond lengths [Å] and angles [°]: Se(1)–Cl(1): 2.556(2), Se(1)–Cl(2): 2.201(3), Se(1)–Cl(3): 2.277(3), Se(1)–Cl(4): 2.766(2), Se(2)–Cl(1): 2.766(3), Se(2)–Cl(4): 2.639(2), Se(2)–Cl(5): 2.189(3), Se(2)–Cl(6): 2.231(3), Se(1)–C(1): 1.961(8), Se(2)–C(7): 1.954(9), C(4)–F(4): 1.362(10), C(10)–F(10): 1.356(10), Cl(1)–Se(1)–Cl(3): 175.29(9), Cl(2)–Se(1)–Cl(4): 172.15(9), Cl(1)–Se(1)–Cl(2): 89.46(9), Cl(2)–Se(1)–Cl(3): 93.56(10), Cl(3)–Se(1)–Cl(4): 91.85(8), Cl(1)–Se(1)–Cl(4): 84.80(7), Cl(1)–Se(2)–Cl(5): 172.60(9), Cl(4)–Se(2)–Cl(6): 172.41(9), Cl(1)–Se(2)–Cl(4): 83.24(7), Cl(1)–Se(2)–Cl(6): 90.51(9), Cl(5)–Se(2)–Cl(6): 94.31(10), Cl(4)–Se(2)–Cl(5): 91.51(9), Se(1)–Cl(1)–Se(2): 96.85(7), Se(1)–Cl(4)–Se(2): 94.92(7).

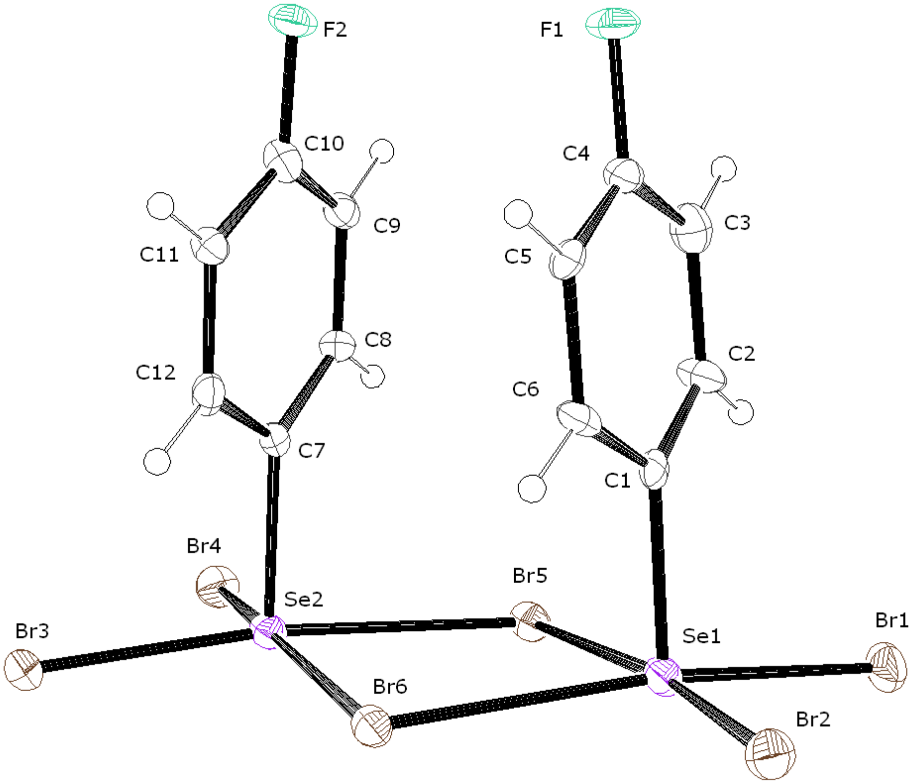

Figure 3 ORTEP representation of the molecular structure of (*p*-FC_6H_4)$SeBr_3$. Thermal ellipsoids are shown at the 30% probability level. Selected bond lengths [Å] and angles [°]: Se(1)–Br(1): 2.401(2), Se(1)–Br(2): 2.374(2), Se(1)–Br(5): 2.885(2), Se(1)–Br(6): 2.822(2), Se(2)–Br(3): 2.453(2), Se(2)–Br(4): 2.374(2), Se(2)–Br(5): 2.716(2), Se(2)–Br(6): 2.896(2), Se(1)–C(1): 1.944(15), Se(2)–C(7): 1.956(16), C(4)–F(1): 1.369(19), C(10)–F(2): 1.337(19), Br(1)–Se(1)–Br(6): 169.33(9), Br(2)–Se(1)–Br(5): 172.95(8), Br(1)–Se(1)–Br(2): 94.32(8), Br(1)–Se(1)–Br(5): 90.42(7), Br(5)–Se(1)–Br(6): 83.18(6), Br(2)–Se(1)–Br(6): 91.34(7), Br(3)–Se(2)–Br(5): 173.09(8), Br(4)–Se(2)–Br(6): 171.45(9), Br(3)–Se(2)–Br(4): 93.28(8), Br(4)–Se(2)–Br(5): 89.23(7), Br(5)–Se(2)–Br(6): 84.85(6), Br(3)–Se(2)–Br(6): 91.93(7), Se(1)–Br(5)–Se(2): 96.87(6), Se(1)–Br(6)–Se(2): 94.27(6).

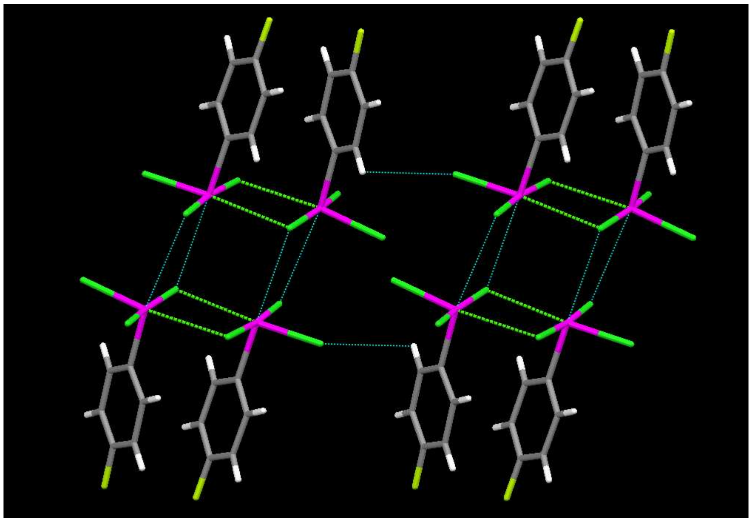

Figure 4 Pairing of dimers via secondary Se···X interactions in the structure of (*p*-FC_6H_4)$SeCl_3$, resulting in distorted octahedral geometry at selenium. These pairs link via C–H···Cl non–classical hydrogen bonds, whilst in (*p*-FC_6H_4)$SeBr_3$ the pairs link by weak Br···Br contacts. Atom and contacts colour code: Carbon (grey), hydrogen (white), fluorine (lime green), chlorine (bright green), selenium (pink). Green lines: intramolecular bridging Se–Cl bonds within dimer, blue dashed lines: weaker Se···Cl or H···Cl intermolecular contacts.

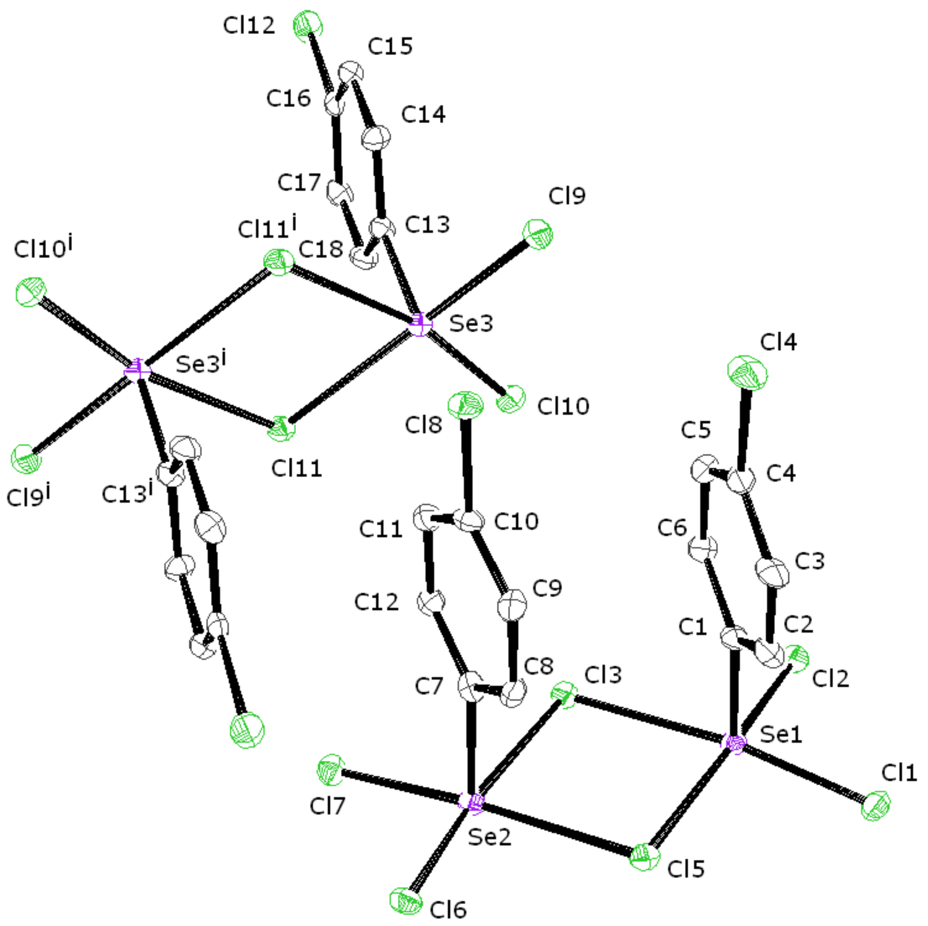

Figure 5 ORTEP representation of the molecular structure of (*p*-ClC$_6$H$_4$)SeCl$_3$. Thermal ellipsoids are shown at the 30% probability level, and hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: Se(1)–Cl(1): 2.250(2), Se(1)–Cl(2): 2.205(2), Se(1)–Cl(3): 2.6225(19), Se(1)–Cl(5): 2.7287(19), Se(2)–Cl(3): 2.7310(19), Se(2)–Cl(5): 2.6201(19), Se(2)–Cl(6): 2.2112(19), Se(2)–Cl(7): 2.240(2), Se(3)–Cl(9): 2.261(2), Se(3)–Cl(10): 2.1949(19), Se(3)–Cl(11): 2.5899(19), Se(3)–Cl(11^{i}): 2.8184(19), Se(1)–C(1): 1.959(7), Se(2)–C(7): 1.948(7), Se(3)–C(13): 1.951(7), C(4)–Cl(4): 1.737(7), C(10)–Cl(8): 1.753(7), C(16)–Cl(12): 1.736(8), Cl(1)–Se(1)–Cl(3): 172.30(7), Cl(2)–Se(1)–Cl(5): 176.72(7), Cl(1)–Se(1)–Cl(2): 93.93(7), Cl(1)–Se(1)–Cl(5): 88.50(7), Cl(3)–Se(1)–Cl(5): 85.69(6), Cl(2)–Se(1)–Cl(3): 91.69(7), Cl(3)–Se(2)–Cl(6): 173.96(7), Cl(5)–Se(2)–Cl(7): 172.76(7), Cl(3)–Se(2)–Cl(5): 85.69(6), Cl(5)–Se(2)–Cl(6): 88.27(7), Cl(6)–Se(2)–Cl(7): 93.32(7), Cl(3)–Se(2)–Cl(7): 92.65(7), Se(1)–Cl(3)–Se(2): 94.25(6), Se(1)–Cl(5)–Se(2): 94.36(6), Cl(9)–Se(3)–Cl(11): 172.31(8), Cl(10)–Se(3)–Cl(11^{i}): 167.94(7), Cl(9)–Se(3)–Cl(10): 94.48(7), Cl(10)–Se(3)–Cl(11): 90.65(7), Cl(11)–Se(3)–Cl(11^{i}): 80.52(6), Cl(9)–Se(3)–Cl(11^{i}): 93.54(6), Se(3)–Cl(11)–Se(3^{i}): 99.48(6). Symmetry operation used to generate equivalent atoms: i: ½-x, ½-y, 1-z.

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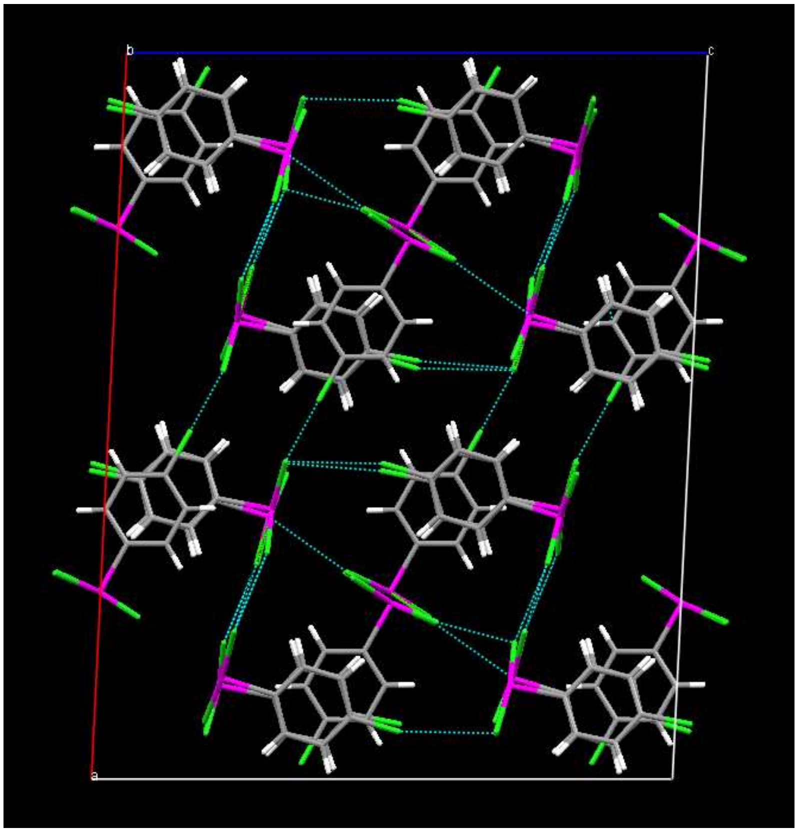

Figure 6 Unit cell of (p-ClC_6H_4)$SeCl_3$ viewed down the crystallographic *b*–axis, showing *cis*– and *trans*–dimers linked by Se···Cl and Cl···Cl contacts. The crystal packing also features extensive offset π–stacking of the aryl rings. Atom and contacts colour code: Carbon (grey), hydrogen (white), chlorine (bright green), selenium (pink). Green lines: intramolecular bridging Se–Cl bonds within dimer, blue dashed lines: weaker Se···Cl or Cl···Cl intermolecular contacts.

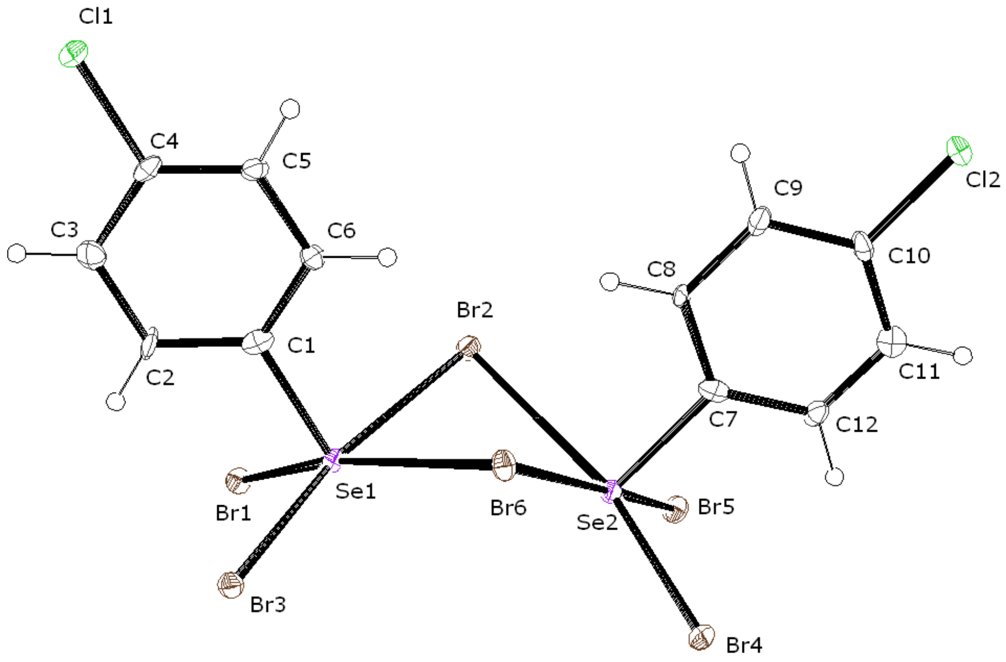

Figure 7 ORTEP representation of the molecular structure of (*p*-ClC_6H_4)$SeBr_3$. Thermal ellipsoids are shown at the 30% probability level. Selected bond lengths [Å] and angles [°]: Se(1)–Br(1): 2.3436(15), Se(1)–Br(3): 2.4479(15), Se(1)–Br(2): 2.6886(15), Se(1)–Br(6): 3.0288(15), Se(2)–Br(4): 2.3693(16), Se(2)–Br(5): 2.4900(15), Se(2)–Br(2): 2.9481(15), Se(2)–Br(6): 2.6520(16), Se(1)–C(1): 1.955(12), Se(2)–C(7): 1.953(11), C(4)–Cl(1): 1.752(11), C(10)–Cl(2): 1.744(12), Br(1)–Se(1)–Br(6): 166.32(5), Br(2)–Se(1)–Br(3): 168.59(6), Br(1)–Se(1)–Br(3): 95.73(5), Br(1)–Se(1)–Br(2): 93.33(5), Br(2)–Se(1)–Br(6): 82.10(4), Br(3)–Se(1)–Br(6): 87.50(4), Br(2)–Se(2)–Br(4): 167.64(5), Br(5)–Se(2)–Br(6): 170.45(6), Br(4)–Se(2)–Br(5): 93.88(5), Br(2)–Se(2)–Br(5): 87.76(4), Br(2)–Se(2)–Br(6): 84.27(4), Br(4)–Se(2)–Br(6): 92.80(5), Se(1)–Br(2)–Se(2): 81.44(4), Se(1)–Br(6)–Se(2): 80.52(4).

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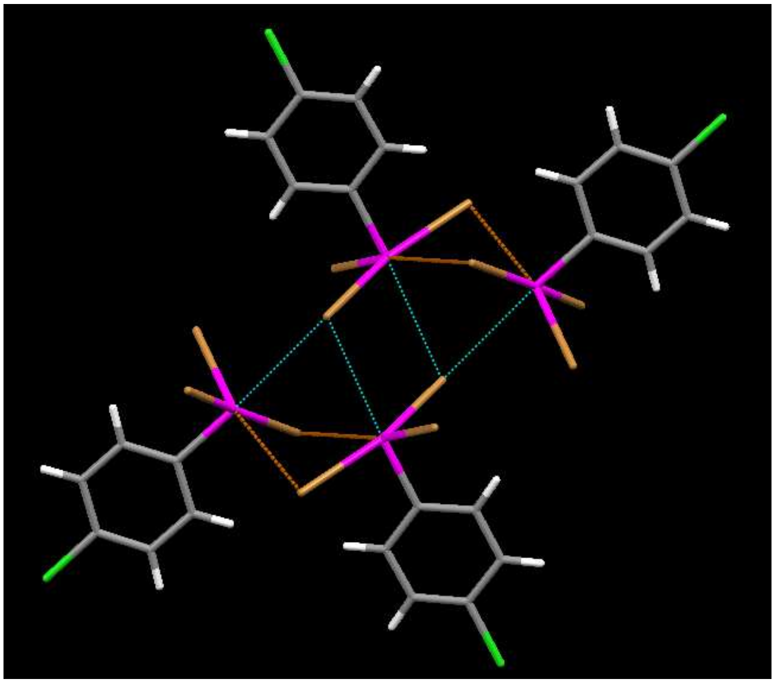


Figure 8 Pairing of folded dimers in the structure of (p–ClC$_6$H$_4$)SeBr$_3$, via Se···Br interactions. Atom / contacts colour code: Carbon (grey), hydrogen (white), chlorine (bright green), bromine (brown), selenium (pink). Brown lines: intramolecular bridging Se–Br bonds within dimer, blue dashed lines: weaker Se···Br intermolecular contacts.

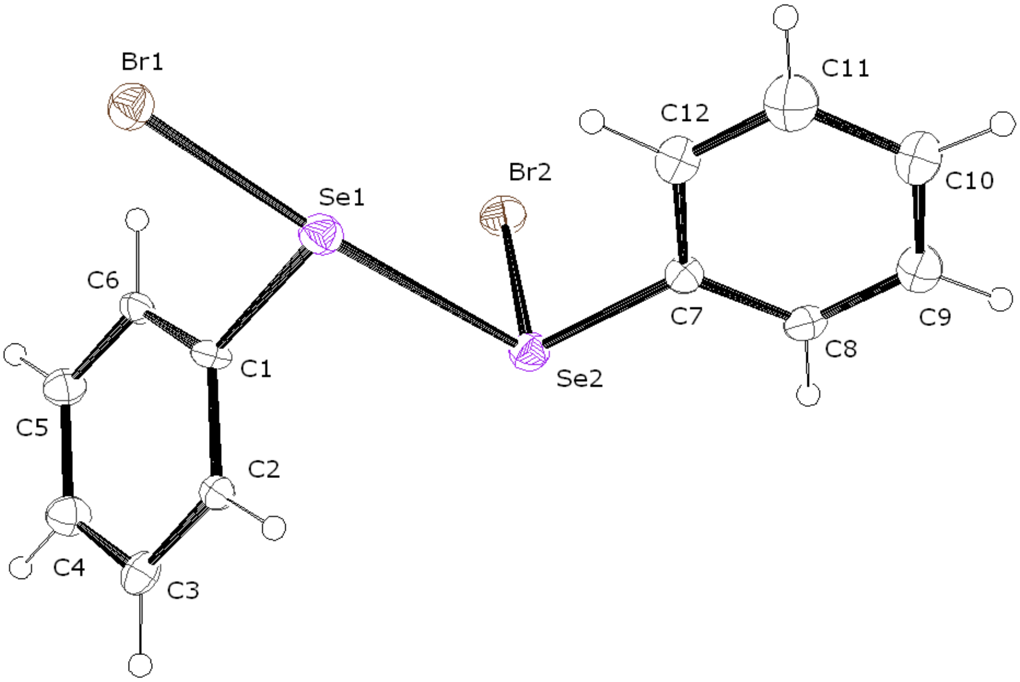


Figure 9 ORTEP representation of the molecular structure of $Ph_2Se_2Br_2$. Thermal ellipsoids are shown at the 30% probability level. Selected bond lengths [Å] and angles [°]: Se(1)–Se(2): 2.832(4), Se(1)–Br(1): 2.449(4), Se(2)–Br(2): 2.352(5), Se(1)–C(1): 1.96(3), Se(2)–C(7): 1.93(3), Br(1)–Se(1)–Se(2): 174.83(19), Br(1)–Se(1)–C(1): 96.4(9), Se(2)–Se(1)–C(1): 85.3(10), Se(1)–Se(2)–Br(2): 93.59(14), Se(1)–Se(2)–C(7): 101.9(10), Br(2)–Se(2)–C(7): 99.3(10).

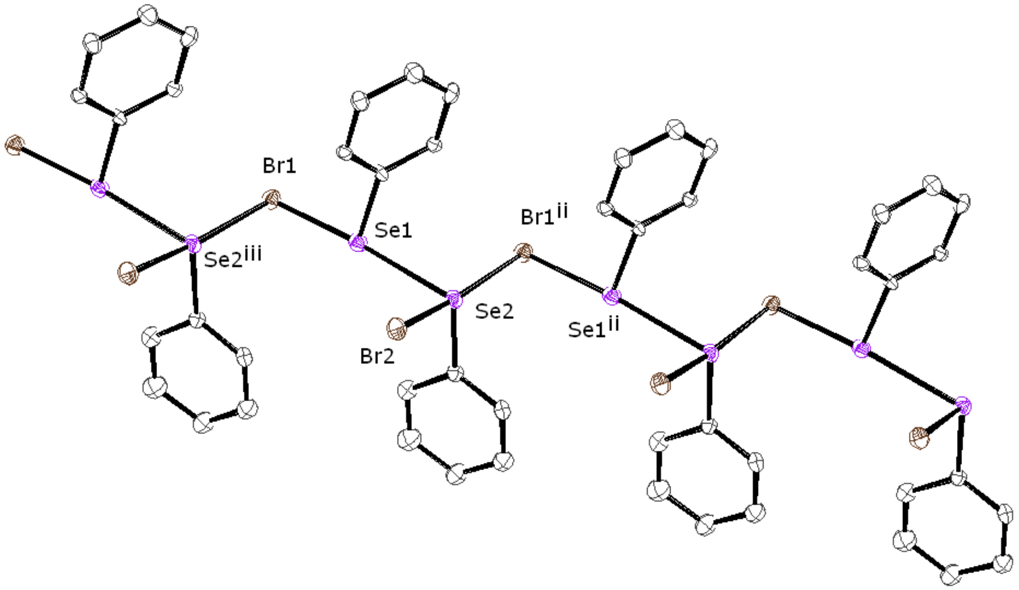


Figure 10 Propagation of chain structure in $Ph_2Se_2Br_2$ via bridging Br(1)···Se(2) interactions of 3.333(4) Å. Hydrogen atoms omitted for clarity. Symmetry operations used to generate equivalent atoms: ii: -1+x, y, z, iii: 1+x, y, z.

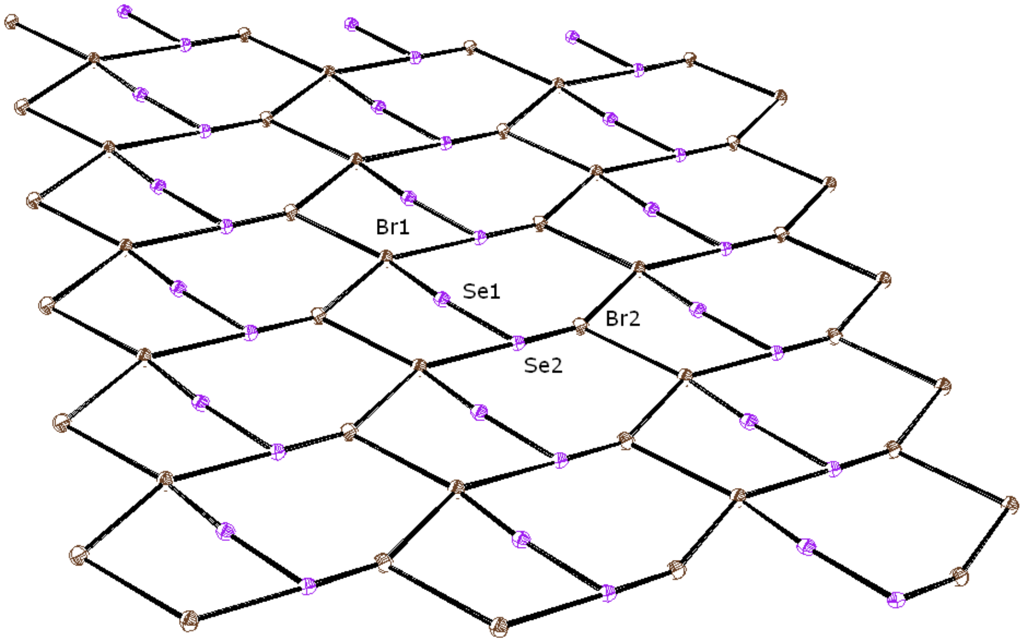


Figure 11 Sheet of selenium and bromine atoms in the extended solid–state structure of $Ph_2Se_2Br_2$. Phenyl rings omitted for clarity.

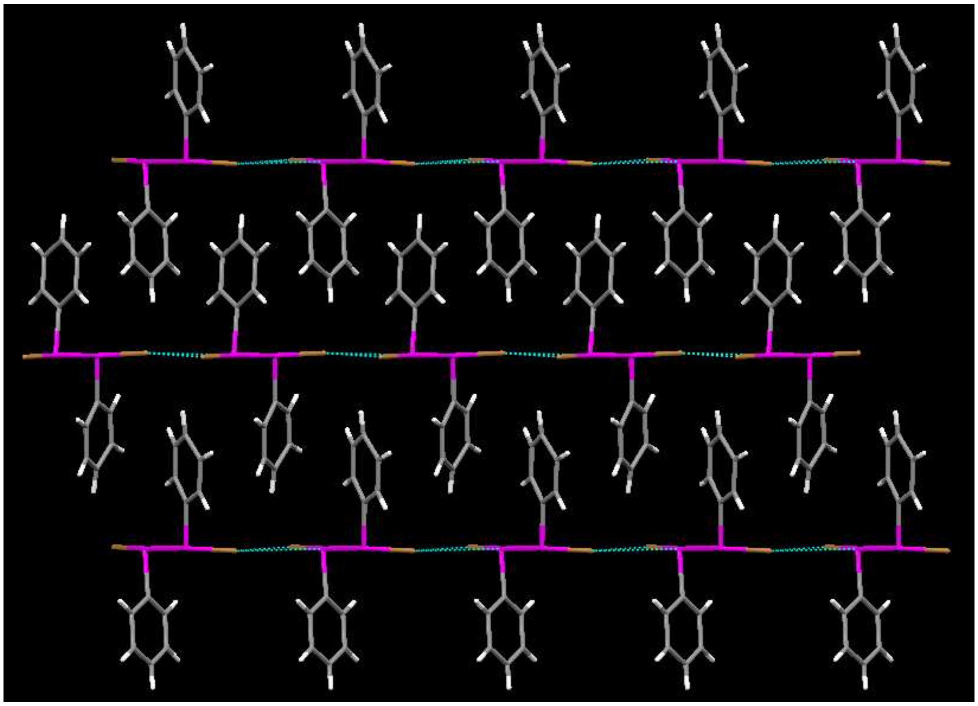


Figure 12 Extended structure of $Ph_2Se_2Br_2$ viewed down the *a*–crystallographic axis, showing the arrangement of stacking of the phenyl rings between essentially planar sheets of selenium and bromine atoms. Atom colour code: Carbon (grey), hydrogen (white), bromine (brown), selenium (pink).

Compound	Se–X bond lengths / Å	Structural type(for $RSeX_3$)	Reference
$PhSeCl_3$	2.198(4)–2.251(5) (*terminal*) 2.616(5)–2.726(5) (*bridging*)	Chain polymer	19
CF_3SeCl_3	2.13(2)–2.25(2) (*terminal*) 2.51(2)–2.75(2) (*bridging*)	*cis*–dimer (folded)	20
1,2–$(SeCl_3)_2C_6H_4$	2.193(4)–2.259(4) (*terminal*) 2.497(3)–2.697(4) (*bridging*)	*cis*–dimer (imposed by bridging C_6H_4 group, Se_2Cl_6 unit is folded)	21
4–$(Me_3Si)_2N$–3,5–$({}^iPr)_2C_6H_2SeCl_3$	2.206(2)–2.257(2) (*terminal*) 2.587(2)–2.749(2) (*bridging*)	*trans*–dimer (planar)	22
{*o*–$(Me_2NCH_2)C_6H_4$}$SeCl_3$	2.3459(9)–2.4349(9) (*terminal*)	Monomer	23
(*p*–FC_6H_4)$SeCl_3$	2.189(3)–2.277(3) (*terminal*) 2.556(2)–2.766(2) (*bridging*)	*cis*–dimer (planar)	This work
(*p*–ClC_6H_4)$SeCl_3$	*cis dimer:* 2.205(2)–2.250(2) (*terminal*) 2.6201(19)–2.7310(19) (*bridging*) *trans dimer:* 2.1949(19)–2.261(2) (*terminal*) 2.5899(19)–2.8184(19) (*bridging*)	Co–crystallized *cis*– and *trans*–dimers (both planar)	This work
$PhSeBr_3$	2.3538(14)–2.3590(13) (*terminal*) 3.0891(13)–3.0976(13) (*secondary*)	Network structure built from [$PhSeBr_2$] fragments and Se···Br and Br···Br interactions.	19
(*p*–FC_6H_4)$SeBr_3$	2.374(2)–2.453(2) (*terminal*) 2.716(2)–2.896(2) (*bridging*)	*cis*–dimer (planar)	This work
(*p*–ClC_6H_4)$SeBr_3$	2.3436(15)–2.4900(15) (*terminal*) 2.6520(16)–3.0288(15) (*bridging*)	*cis*–dimer (folded)	This work
$[Ph_4As]_2[Se_2Cl_{10}]$	2.217(3)–2.306(3) (*terminal*) 2.519(2)–2.803(3) (*bridging*)		36
$[Ph(NH_2)C{=}NC(Ph)NHCl]_2[Se_2Cl_{10}]$	2.208(2)–2.210(2) (*terminal*) 2.725(2)–2.733(2) (*bridging*)		37
$[Et_4N]_2[Se_2Cl_{10}]$	2.205(3)–2.265(3) (*terminal*) 2.576(3)–2.799(3) (*bridging*)		38
$[S_4N_3]_2[Se_2Cl_{10}]$	2.189(2)–2.222(3) (*terminal*) 2.688(2)–2.816(3) (*bridging*)		39
$[Et_4N]_2[Se_2Br_{10}]$	2.393(3)–2.432(4) (*terminal*) 2.756(4)–2.877(4) (*bridging*)		33

$[C_4H_{10}NO]_2[Se_2Br_{10}]$	2.369(1)–2.390(1) (*terminal*) 2.871(1)–2.923(1) (*bridging*)	40

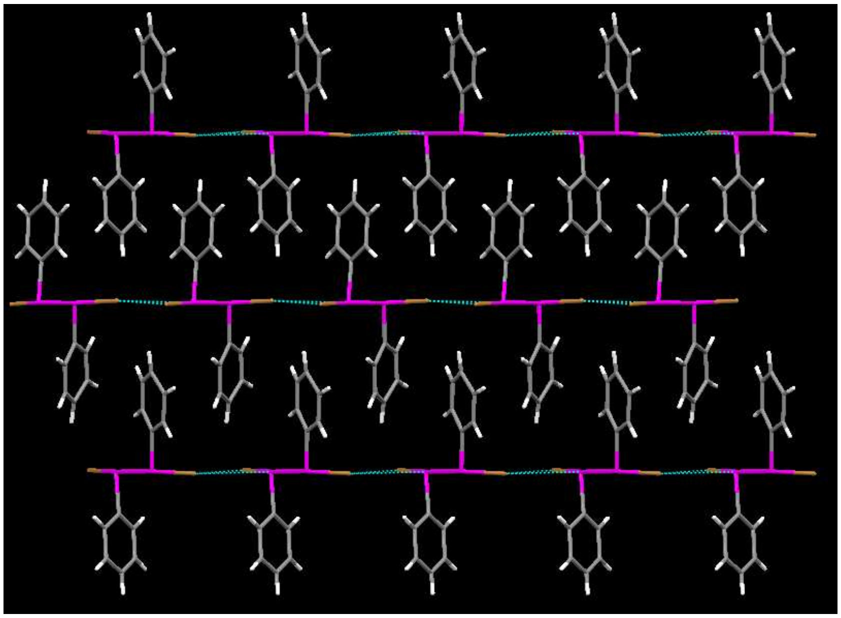
Table 1 Comparison of terminal and bridging Se–X bond lengths in structures of $RSeX_3$ compounds, and related $[Se_2X_{10}]^{2-}$ anions (X = Cl, Br).

	(p–FC_6H_4)$SeCl_3$	(p–FC_6H_4)$SeBr_3$	(p–ClC_6H_4)$SeCl_3$
Empirical formula	$C_{12}H_8Cl_6F_2Se_2$	$C_{12}H_8Br_6F_2Se_2$	$C_{18}H_{12}Cl_{12}Se_3$
Fw	560.80	827.56	890.56
Colour, habit	Colourless, block	Orange, block	Colourless, prism
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$C2/c$ (no. 15)	$C2/c$ (no. 15)	$C2/c$ (no. 15)
Crystal size	0.12 x 0.12 x 0.05 mm^3	0.04 x 0.06 x 0.10 mm^3	0.12 x 0.12 x 0.06 mm^3
Unit cell dimensions	a = 17.4590(6) Å, α = 90° b = 8.7778(3) Å, β = 100.7710(10)° c = 23.2622(9) Å, γ = 90°	a = 17.7188(6) Å, α = 90° b = 9.1035(3) Å, β = 97.236(1)° c = 23.4934(11) Å, γ = 90°	a = 25.4102(7) Å, α = 90° b = 10.7139(3) Å, β = 92.780(2)° c = 20.2732(6) Å, γ = 90°
Volume	3502.2(2) $Å^3$	3759.4(3) $Å^3$	5512.7(3) $Å^3$
T	100(2) K	100(2) K	100(2) K
Z	8	8	8
$D_{\text{calcd.}}$	2.127 mg/m^3	2.924 mg/m^3	2.146 mg/m^3
λ	0.71073 Å	0.71073 Å	0.71073 Å
μ (Mo-Kα)	5.147 mm^{-1}	16.698 mm^{-1}	5.178 mm^{-1}
F(000)	2144	3008	3408
θ range	3.23 to 26.00°	2.98 to 25.70°	3.07 to 25.50°
No. of reflections	12163 (3423 unique)	19016 (3551 unique)	20467 (5108 unique)
R_{int}	0.088	0.117	0.081
$R1$ / $wR2$	0.0664 / 0.1543	0.0803 / 0.1792	0.0567 / 0.1326
$R1$ / $wR2$ (all data)	0.1067 / 0.1773	0.1272 / 0.2001	0.0902 / 0.1554
Largest diff. peak and hole	1.469 and –0.934 $eÅ^{-3}$	1.645 and –2.752 $eÅ^{-3}$	1.982 and –1.103 $eÅ^{-3}$
GOF	1.276	1.272	1.037

Table 2 Crystallographic parameters for compounds (p–FC_6H_4)$SeCl_3$, (p–FC_6H_4)$SeBr_3$, (p–ClC_6H_4)$SeCl_3$, (p–ClC_6H_4)$SeBr_3$ and $Ph_2Se_2Br_2$.

	(p–ClC_6H_4)$SeBr_3$	$Ph_2Se_2Br_2$
Empirical formula	$C_{12}H_8Br_6Cl_2Se_2$	$C_{12}H_{10}Br_2Se_2$
Fw	860.46	471.94
Colour, habit	Orange, plate	Purple, prism
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$ (no. 14)	$P2_1$ (no. 4)
Crystal size	0.02 x 0.14 x 0.14 mm^3	0.05 x 0.05 x 0.12 mm^3
Unit cell dimensions	a = 7.2480(1) Å, α = 90° b = 25.3497(5) Å, β = 96.980(1)° c = 10.7265(3) Å, γ = 90°	a = 6.0108(5) Å, α = 90° b = 7.1843(7) Å, β = 90.004(4)° c = 15.6165(18) Å, γ = 90°
Volume	1956.22(7) $Å^3$	674.37(12) $Å^3$
T	100(2) K	100(2) K
Z	4	2
$D_{\text{calcd.}}$	2.921 mg/m^3	2.324 mg/m^3
λ	0.71073 Å	0.71073 Å
μ (Mo-Kα)	16.301 mm^{-1}	11.378 mm^{-1}
F(000)	1568	440
θ range	2.94 to 26.00°	3.63 to 25.60°
No. of reflections	21237 (3805 unique)	5484 (2061 unique)
R_{int}	0.0696	0.158
$R1$ / $wR2$	0.0670 / 0.1660	0.0866 / 0.2130
$R1$ / $wR2$ (all data)	0.0821 / 0.1756	0.1222 / 0.2544
Largest diff. peak and hole	1.881 and –2.760 $eÅ^{-3}$	2.487 and –2.202 $eÅ^{-3}$
GOF	1.138	1.068

Table 2 (cont.) Crystallographic parameters for compounds (p–FC_6H_4)$SeCl_3$, (p–FC_6H_4)$SeBr_3$, (p–ClC_6H_4)$SeCl_3$, (p–ClC_6H_4)$SeBr_3$ and $Ph_2Se_2Br_2$.



Structural isomerism in (p–XC$_6$H$_4$)SeCl$_3$ and (p–XC$_6$H$_4$)SeBr$_3$ (X = F, Cl) compounds. Co–crystallisation of *cis*– and *trans*– dimeric forms of (p–ClC$_6$H$_4$)SeCl$_2$(μ–Cl)$_2$(p–ClC$_6$H$_4$)SeCl$_2$. A new structural modification for the "PhSeBr" reagent, Ph$_2$Se$_2$Br$_2$, containing an elongated Se–Se bond.

Nicholas A. Barnes, Stephen M. Godfrey, Ruth T. A. Ollerenshaw, Rana Z. Khan and Robin G. Pritchard

Structural isomerism has been observed for the selenium(IV) compounds (p-XC$_6$H$_4$)SeCl$_3$ and (p-XC$_6$H$_4$)SeBr$_3$ (X = F, Cl), which may adopt dimeric structures which are either *cis*–planar, *cis*–folded, or, in the case of (p-ClC$_6$H$_4$)SeCl$_3$, both *cis* and *trans*–dimers are found to co–crystallise in the unit cell. A new structural modification of "PhSeBr" is also reported, which is dimeric, Ph$_2$Se$_2$Br$_2$, with an elongated Se–Se bond.