Review Article

The Nature of the Chemical Bond in Linear Three-Body Systems: From $I_3^-$ to Mixed Chalcogen/Halogen and Trichalcogen Moieties

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The 3 centre-4 electrons (3c-4e) and the donor/acceptor or charge-transfer models for the description of the chemical bond in linear three-body systems, such as $I_3^-$ and related electron-rich (22 shell electrons) systems, are comparatively discussed on the grounds of structural data from a search of the Cambridge Structural Database (CSD). Both models account for a total bond order of 1 in these systems, and while the former fits better symmetric systems, the latter describes better strongly asymmetric situations. The 3c-4e MO scheme shows that any linear system formed by three aligned closed-shell species (24 shell electrons overall) has reason to exist provided that two electrons are removed from it to afford a 22 shell electrons three-body system: all combinations of three closed-shell halides and/or chalcogenides are considered here. A survey of the literature shows that most of these three-body systems exist. With some exceptions, their structural features vary continuously from the symmetric situation showing two equal bonds to very asymmetric situations in which one bond approaches to the value corresponding to a single bond and the second one to the sum of the van der Waals radii of the involved atoms. This indicates that the potential energy surface of these three-body systems is fairly flat, and that the chemical surrounding of the chalcogen/halogen atoms can play an important role in freezing different structural situations; this is well documented for the $I_3^-$ anion. The existence of correlations between the two bond distances and more importantly the linearity observed for all these systems, independently on the degree of their asymmetry, support the state of hypervalency of the central atom.

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1. INTRODUCTION

The chemical bond in linear three-body systems, such as trihalides, has been the object of many papers appeared very recently in the literature [1–5]. Among them, the paper on trihalides and hydrogen dihalides published by Hoffmann et al. [2], the book edited by Akiba [1] “Chemistry of hypervalent compounds” appeared in 1999, and the chapter on hypervalent chalcogen compounds by Nakanishi [4] in “Handbook of chalcogen chemistry” edited by F. A. Devillanova, represent authoritative contributions to this topic. In particular, the paper by Hoffman analyzes, on the basis of theoretical calculations, the various contributions to the stabilization of trihalides, by comparing the Rundle-Pimentel [6, 7] model for electron-rich 3-centre 4-electron systems (Scheme 1) with that describing the interhalogenic bond as a donor/acceptor or charge-transfer interaction between a halide and a dihalogen molecule (Scheme 2).

The commonly accepted 3 centre-4 electron bonding model considers the central halogen to be hypervalent. According to this model, a linear system formed for example by three aligned closed-shell $I^-$ (24 shell electrons overall, $I_3^-$) has no reason to exist since the three MOs generated by the combination of the three $p_z$ orbitals, one from each interacting anion (Scheme 1), should be fully occupied by six electrons. However, the removal of two electrons from the antibonding MO causes an effective stabilization of the system and affords the well-known 22 shell electrons $I_3^-$ anion (Scheme 1). The stability of $I_3^-$ is determined by the occupancy of the lowest MO since the second filled MO is non-bonding in nature. The four electrons on the $\sigma$ MOs plus the 6 electrons on the other three filled atomic orbitals equal a
total of 10 electrons on the central I atom; this accounts for its description as an hypervalent species. However, a more formal counting indicates that only 8 electrons can be assigned to the central iodine since the HOMO is a combination out of phase of the \( p_z \) orbitals of the external iodine atoms; consequently, no electron density coming from this MO can be assigned to the central iodine.

The alternative description of \( I_3^- \) according to a Lewis model, which considers an \( sp^2 \) \( I^+ \) cation having three lone pairs on the plane perpendicular to the bond direction and two hybrid orbitals able to linearly coordinate two \( I^- \) anions (Scheme 3), leads again to assign 10 electrons to the central iodine.

However, this model implies the combination of the \( d_{2z^2} \) and \( p_z \) atomic orbitals of the central \( I^+ \) to afford two unfilled hybrid orbitals able to accommodate two lone pairs from the two \( I^- \) anions. According to this description, a simple notation, introduced by Arduengo et al. [5], identifies the central I atom as a 10-I-2 species, where “10” indicates the number of the electrons around the central \( I \), and “2” the number of the atoms or groups bonded to it. We must note that this formalism accounts very well for the hypervalent nature (expansion of the octet) of the central iodine, but does not account for the strength of the two bonds formed; in fact, according to such a model, each bond, arising from the localization of a pair of electrons from \( I^- \), should have a bond order of 1.

The simplest way to prepare a triiodide or in general a trihalide species considers the reaction between an \( X^- \) anion with an \( X_2 \) molecule (\( X^- + X_2 \rightarrow X_3^- \)). In terms of chemical bond description, this corresponds to the commonly named donor/acceptor interaction (Scheme 2) since the bond is formed via a \( \sigma \) donation from one of the four filled atomic orbitals of \( X^- \) (\( np \)) towards the empty \( \sigma^* \) anti-bonding molecular orbital of \( X_2 \). As \( X^- \) formally approaches \( X_2 \), the three lone pairs of the approached \( X \) atom of the \( X_2 \) molecule are reoriented in order to be on the plane perpendicular to the bond direction when the symmetric three-body system \( X_3^- \) is formed. It corresponds to the rearrangement of a \( sp^3 \) carbon atom during a nucleophilic attack in an SN2 type reaction (Scheme 4). The substantial difference between a trihalide and a penta-coordinated carbon resides in their different stabilities: while the penta-coordinated carbon represents a transition state, which finds its stabilization by removing one of the two apical groups so to allow the carbon to return to an \( sp^3 \) hybridization, \( X_3^- \) is a stable species. In such systems, the counting of the electrons around the central halogen and carbon atoms agrees very well with the notation by Arduengo et al. [5] (10-X-2 and 10-C-5, resp.). In fact, since the starting diatomic species (\( X_2 \) in the case of trihalides formation) obeys to the octet rule, every interaction with a donor (\( X^- \) in the case of trihalides formation) implies a transfer of electron density on \( X_2 \), thus formally justifying a number of electrons higher than 8 on the central atom of the resulting three-body system.

The simplified donor/acceptor first approximation MO diagram for the formation of a trihalide species (Scheme 2) becomes more complicated if the donor atomic orbital of \( X^- \) (\( np \)) is combined with both the \( \sigma^* \) and the \( \sigma^b \) MOs of \( X_2 \). The result is a second approximation MO diagram having three new energy levels for the adduct, coming from the combination of these three orbitals (Scheme 3).1

The difference between the first and second approximation MO diagrams (Schemes 2 and 5) resides in the nature of the first two MOs of the formed three-body system. In fact, the energy mixing in the second approximation diagram

1 However, in the construction of the simplified MO diagram for the donor/acceptor interaction (first approximation; Scheme 2), the combination of the donor orbital with only the \( \sigma^* \) MO of \( X_2 \), leaving unchanged the \( \sigma^b \) level, is justified fairly well by a good match of energy between the lone pair of \( X^- \) and the \( \sigma^* \) MO of \( X_2 \).
Model, involving only the combination of a lone pair of $X^-$ of the two bonds formed. According to the charge-transfer model, the stabilisation of electron-rich (22 shell electrons) closed-shell fragments; the stabilization is reached by removing a couple of electrons in order to leave unfilled the highest MO (Scheme 1). Scheme 1 shows the combination of three $p$ orbitals lying at the same level of energy; in a more general scheme with different starting closed-shell fragments, the combined $p$ orbitals lie at different energy levels with the consequence that they will contribute differently to each molecular orbital in the resulting three-body system. In particular, if the combined $p$ orbital of one of the two external atoms lies at an energy level quite different from that of the $p$ orbitals of the other two atoms, its contribution to the bonding MO will be poor with a consequent unbalancing of the two bonds. This case is normally better described with the charge-transfer model, which corresponds to the interaction between a donor and a 2c-2e bond system.

Another aspect that we must consider is the total charge brought by the final three-body system; it will depend only on the charges of the starting aligned closed-shell species. A very simple example is represented by the formation of the XeF$_2$ molecule according to a 3c-4e model: the three-closed shell species to be considered are 2 $^-$ and Xe; by removing a couple of electrons the neutral XeF$_2$ molecule is generated. When three equal or different $X^-$ ($X^- = \text{halide}$) are aligned, the resulting three-body system will be a trihalide monoanion.

The situation is much more complex for the formation of three-body systems from closed-shell species of 16th group elements, since the closed-shell species which can be combined can be both charged ($E^-$, $R^-E^-$) and neutral ($R_2E$ and $R=E$, $R = \text{organic framework}$ and $E = \text{chalcogen atom}$). In general, the alignment of three identical chalcogen species can afford three-body systems featuring very different charges, (a)–(d) in Scheme 6.

In principle, any combination of $E^2$, $R^2E$, $R_2E$, and $R=E$ species is possible, thus strongly increasing the variety of obtainable three-body systems. In addition, the central chalcogen atom of the three-body systems (a)–(d) reported in Scheme 6 can be aligned in turn to one or two other couples of closed-shell chalcogen species to form, after removal of 1 or 2 couples of electrons, systems featuring two ($\text{or}$) in Scheme 6) or three orthogonal 3c-4e fragments, respectively. In this way we can explain the great variety of structural archetypes which contain a hypervalent chalcogen atom. The number of possible combinations further increases if mixed S, Se, and Te systems are also taken into account (see below).

Analogously to asymmetric trihalides, many asymmetric trichalcogen and mixed dichalcogen/halogen and chalcogen/dihalogen systems can be successfully described using the same charge-transfer model as that used for asymmetric trihalides. According to this model three-body systems arise from the interaction between a donor species (halide or chalcogen) and an acceptor species (dihalogen, ...

\begin{equation}
(Scheme 5) \text{ has the consequence of increasing the bonding nature of the lowest MO, moving the intermediate MO to higher energies towards a nonbonding nature. Now we can compare the 3c-4e bond model (Scheme 1) with the two MO diagrams for the donor/acceptor interaction between X$^-$ and X$_2$ (Schemes 2 and 5) to describe the chemical bond in X$_3^-$ anions. Since in all the three schemes, the highest MO is always an antibonding molecular orbital featuring a nodal plane between each couple of atoms, the differences between these models are mainly determined by the different nature of the lowest two molecular orbitals. According to the 3c-4e model, the stabilisation of electron-rich (22 shell electrons) three-body systems has to be ascribed only to the filling of the lowest MO, with a consequent bond order of 0.5 for each of the two bonds formed. According to the charge-transfer model, involving only the combination of a lone pair of X$^-$ with the $\sigma^*$ MO of X$_2$, the filling up of the lowest energy level corresponds to a bond order of 1 within the X$_2$ fragment, while the filling up of the intermediate level accounts for the bond formation between the two interacting fragments and for a lengthening of the X–X bond in X$_2$; a bond order of 0.5 for both bonds is reached in the symmetric situation X–X–X$^-$. In the second approximation charge-transfer MO diagram (Scheme 5), the lone pair of X$^-$ combines with both $\sigma^b$ and $\sigma^*$ MOs of X$_2$, consequently the bonding nature of first molecular orbital of the resulting three-body system is increased, and that of the second energy level is decreased, thus making this MO diagram intermediate between the 3c-4e and the first approximation charge-transfer MO diagrams (Schemes 1, 2, and 5).

\section{2. Discussion}

The two bonding models (3c-4e and charge-transfer models) can be successfully employed to describe the chemical bond in numerous linear three-body systems featuring 22 shell electrons, formed by three aligned main group elements. The 3c-4e model describes linear three-body systems (electron-rich linear systems) in terms of interacting aligned closed-shell fragments; the stabilization is reached by removing a couple of electrons in order to leave unfilled the highest MO (Scheme 1). Scheme 1 shows the combination of three $p$ orbitals lying at the same level of energy; in a more general scheme with different starting closed-shell fragments, the combined $p$ orbitals lie at different energy levels with the consequence that they will contribute differently to each molecular orbital in the resulting three-body system. In particular, if the combined $p$ orbital of one of the two external atoms lies at an energy level quite different from that of the $p$ orbitals of the other two atoms, its contribution to the bonding MO will be poor with a consequent unbalancing of the two bonds. This case is normally better described with the charge-transfer model, which corresponds to the interaction between a donor and a 2c-2e bond system.

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Analogously to asymmetric trihalides, many asymmetric trichalcogen and mixed dichalcogen/halogen and chalcogen/dihalogen systems can be successfully described using the same charge-transfer model as that used for asymmetric trihalides. According to this model three-body systems arise from the interaction between a donor species (halide or chalcogen) and an acceptor species (dihalogen, ...

\begin{equation}
Scheme 6: Different three-body systems featuring aligned chalcogen atoms. In (e) L = N-methylbenzothiazole-2(3H)-selone.

dichalcogen, or chalcogen-halogen). Therefore, a trichalcogen arrangement derives from the $n(E)\rightarrow\sigma^*(E-E)$ interaction between one of the above-mentioned closed-shell chalcogen species acting as a donor and the empty $\sigma^*$ MO of a dichalcogen molecule acting as an acceptor. In the case of mixed halogen/chalcogen systems, depending on the starting species, different topologies of three-body systems can be obtained, such as $E-X-Y$, $X-E-Y$, $E-E-X$, and $E-X-E$ ($E$ = chalcogen, $X$, $Y$ = halogen), which correspond to the well-known charge-transfer adducts between chalcogen donors and dihalogens ($E-X-Y$), “T-shaped” adducts of chalcogen donors ($X-E-Y$), dichalcogen molecules interacting with halides ($E-E-X$), and halogen(+) linearly coordinated by two chalcogen donor molecules ($E-X-E$).

3. TRIHALIDES

The Cambridge Structural Database (CSD) has been searched for discrete trihalides fragments contained in deposited crystal structures; the results of the search are collected in Table 1.

The triiodides are the most numerous and the scatter plot of the corresponding two I–I bond lengths is shown in Figure 1.

The literature related to triiodides has been omitted here and we refer to the paper by Svensson and Kloo [3]. Although several data are spread apart in the scatter plot, the majority of them are concentrated in the region corresponding to symmetric or weakly asymmetric triiodides. It is important to point out that an analogous correlation is found for $Br_3^-$ anions (see Figure 2) [44–109] while for other trihalides, such as $ICl_2^-$ (Figure 3) [115–152] and $IBr_2^-$ (Figure 4)
Table 1: Occurrence of linear isolated trihalide $X−Y−Z$ fragments crystallographically characterized from a search of the Cambridge Structural Database (number of crystal structures in parentheses).

<table>
<thead>
<tr>
<th>$X=\ast$</th>
<th>$Y−Z=\ast$</th>
<th>$I−I$</th>
<th>$I−Br$</th>
<th>$I−Cl$</th>
<th>$Br−Br$</th>
<th>$Br−Cl$</th>
<th>$Cl−Cl$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>809 (608)$^{(a)}$</td>
<td>*</td>
<td>*</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Br</td>
<td>5$^{(b)}$</td>
<td>56 (40)$^{(c)}$</td>
<td>*</td>
<td>86 (71)$^{(d)}$</td>
<td>—</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>2$^{(e)}$</td>
<td>4$^{(f)}$</td>
<td>55 (46)$^{(g)}$</td>
<td>1$^{(h)}$</td>
<td>6$^{(i)}$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^{(a)}$For the references of triiodides see [3]. $^{(b)}$References [8–11]. $^{(c)}$References [12–43]. $^{(d)}$References [15, 44–109]. $^{(e)}$References [10, 110, 111]. $^{(f)}$References [112–114]. $^{(g)}$References [32, 35, 43, 110, 111, 114–152]. $^{(h)}$Reference [153]. $^{(i)}$References [154–160]. $\ast$These fragments are already considered in the table.

Table 2: Structural features of all the less common $X−Y−Z$ linear trihalides characterized by X-ray diffraction analysis.

<table>
<thead>
<tr>
<th>Compound reference code</th>
<th>$X$</th>
<th>$Z$</th>
<th>$Y$</th>
<th>$d(X−Z)$ (Å)</th>
<th>$d(Z−Y)$ (Å)</th>
<th>$\angle X−Z−Y(\ast)\ast$</th>
<th>References</th>
</tr>
</thead>
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<tr>
<td>CUPTIQ</td>
<td>Cl</td>
<td>Cl</td>
<td>Cl</td>
<td>2.182</td>
<td>2.394</td>
<td>177.7</td>
<td>[154, 155]</td>
</tr>
<tr>
<td>DEGLIK</td>
<td>Cl</td>
<td>Cl</td>
<td>Cl</td>
<td>2.248</td>
<td>2.338</td>
<td>177.5</td>
<td>[156]</td>
</tr>
<tr>
<td>PHASCL</td>
<td>Cl</td>
<td>Cl</td>
<td>Cl</td>
<td>2.227</td>
<td>2.306</td>
<td>177.4</td>
<td>[157]</td>
</tr>
<tr>
<td>UHUQAP</td>
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<td>Cl</td>
<td>Cl</td>
<td>2.144</td>
<td>2.419</td>
<td>178.1</td>
<td>[158]</td>
</tr>
<tr>
<td>ZEHTIP</td>
<td>Cl</td>
<td>Cl</td>
<td>Cl</td>
<td>2.262</td>
<td>2.307</td>
<td>178.4</td>
<td>[160]</td>
</tr>
<tr>
<td>TEACBR</td>
<td>Cl</td>
<td>Br</td>
<td>Cl</td>
<td>2.379</td>
<td>2.401</td>
<td>176.8</td>
<td>[153]</td>
</tr>
<tr>
<td>DOBUTUJ</td>
<td>Cl</td>
<td>I</td>
<td>Br</td>
<td>2.648</td>
<td>2.651</td>
<td>179.6</td>
<td>[112]</td>
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<tr>
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<td>I</td>
<td>Br</td>
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<td>2.675</td>
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<td>[113]</td>
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<td>I</td>
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<td>179.6</td>
<td>[114]</td>
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<td>I</td>
<td>Br</td>
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<td>179.8</td>
<td>[114]</td>
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<tr>
<td>BEQXEA</td>
<td>I</td>
<td>I</td>
<td>Cl</td>
<td>2.737</td>
<td>3.040</td>
<td>172.1</td>
<td>[110]</td>
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<tr>
<td>LACPUB</td>
<td>I</td>
<td>I</td>
<td>Cl</td>
<td>2.765</td>
<td>2.739</td>
<td>179.3</td>
<td>[111]</td>
</tr>
<tr>
<td>EKIHHEL</td>
<td>I</td>
<td>I</td>
<td>Br</td>
<td>2.890</td>
<td>2.906</td>
<td>178.7</td>
<td>[8]</td>
</tr>
<tr>
<td>EYOVAP</td>
<td>I</td>
<td>I</td>
<td>Br</td>
<td>2.857</td>
<td>2.950</td>
<td>179.3</td>
<td>[9]</td>
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<tr>
<td>LACQAI</td>
<td>I</td>
<td>I</td>
<td>Br</td>
<td>2.775</td>
<td>2.856</td>
<td>178.7</td>
<td>[10]</td>
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<tr>
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<td>I</td>
<td>Br</td>
<td>2.780</td>
<td>2.857</td>
<td>176.6</td>
<td>[10]</td>
</tr>
<tr>
<td>WOPGOX</td>
<td>I</td>
<td>I</td>
<td>Br</td>
<td>2.786</td>
<td>2.794</td>
<td>179.2</td>
<td>[11]</td>
</tr>
</tbody>
</table>

$\ast$The angle values are rounded off to the first decimal digit.
strongly elongated with respect to the sum of the covalent radii (2.39 Å) [161] but remain fairly shorter than the sum of the van der Waals radii (3.73 Å) [161]. The structural features of I−I−Cl− and I−I−Br− (Table 2) indicate that the bond distance of the central atom with the lighter halogen is always longer than the I−I distance, in accordance with a different ionic character of the two bonds. In terms of the 3c-4e model (Scheme 1), the p orbitals of the two terminal halogens do not contribute equally to the three molecular orbitals of the three-body systems I−I−X− (X = Cl, Br, I). In fact, the p orbital of the terminal atom featuring the better energy match with the p orbital of the central halogen will contribute more to the bonding MO; vice versa, the other halogen will mainly contribute to the nonbonding MO, thus carrying most of the negative charge. As a consequence, the bond orders of the two bonds diverge from the value of 0.5, one increasing towards the value of 1 (I−I), and the other decreasing towards the value of 0 (I−X). In terms of the charge-transfer model (Scheme 2), asymmetric trihalides of the type X−Z· · · Y− derive from the donor/acceptor interaction between the halide (Y−) and the acceptor species (X−Z); the strength of this interaction will depend on the reciprocal energy levels of the combining orbitals (p of the halide and σ* MO of the dihalogen molecule).

However, in all trihalides, independently of the different polarization of the two bonds the sum of the bond lengths (dx−x + dy−y) is always at least 9% longer than the sum of the covalent radii of the involved atoms, thus indicating a hypervalent state of the central halogen.

4. TRICHALCOGEN(IDE)S

Table 3 collects the occurrence of linear E−E′−E′′ (E, E′, E′′ = chalcogen atom) trichalcogen organic fragments found in structurally characterized compounds, as retrieved from a search of the Cambridge Structural Database (CSD) by imposing either the presence of two covalent bonds between the chalcogen atoms or the presence of one covalent bond and a nonbonding contact shorter than Σvdw − 0.3 Å (E· · · E′−E′′ and E′− · · · E′′ fragments). In both searches, the linearity of the fragment has been imposed (∠E−E′−E′′ > 165°).

As one can see, some combinations of trichalcogen systems have never been reported and some others have been found only in a limited number of structures (Table 4).

The scatter plots of d(E−E′) versus d(E′−E′′) for all trichalcogen fragments present in numerous crystal structures are shown in Figures 5–9.

Similar to what found for trihalides, linear trichalcogen systems can vary from symmetric to very asymmetric ones, but always feature strongly correlated d(E−E′) and d(E′−E′′) bond lengths. This indicates that also in linear trichalcogen E−E′−E′′ organic fragments the potential energy hole should be fairly flat, being the chemical surrounding of the chalcogen atoms and the crystal packing effects able to freeze different structural situations. As mentioned above, in the case of 16th group elements, different closed-shell chalcogen species can interact to afford different types of linear trichalcogen systems (Scheme 6). However, since the analysis of all linear trichalcogen systems would go beyond the aim of this work, we will focus our attention only on some of them. When the closed-shell species are three E2− anions, the corresponding three-body systems will be E3+−. Indeed, the linear Te3+4−, together with the “T-shaped” TeTe4−, and the square-planar TeTe4− anions are considered fundamental building units of numerous polytellurides [359]. The Te−Te bond distances in such tellurides show elongation of about 13% with respect to the sum of the covalent radii and are typical for 3c-4e bonds [359]. A symmetric (Se5)3− ion was identified for the first time in the samarium/selenide cluster [[(C6Me5)Sm]6Se11] [334], and considered a species isoelectronic to I3−. The Se−Se bond length in this system (2.749 Å) is much longer than the mean bond length in (Se2)32− species (2.37 Å). This was justified by analogy with the couple I3−/I−. Linear [E−E· · · E]3+ systems (E = S, Se) have been found in Mo and W clusters

Figure 3: Scatter plot of d1 versus d2 for linear (angle > 165°) iododichlorides from a search of the CSD (46 structures containing 56 fragments). The mean bond lengthening is 9.2% with respect to the sum of the covalent radii.

Figure 4: Scatter plot of d1 versus d2 for linear (angle > 165°) iododibromides from a search of the CSD (40 structures containing 56 fragments). The mean bond lengthening is 9.7% with respect to the sum of the covalent radii.
Table 3: Occurrence of linear trichalcogen E−E′−E′′, E···E′−E′′, and E−E′···E′′ fragments crystallographically characterized from a search of the Cambridge Structural Database (number of crystal structures in parentheses).

<table>
<thead>
<tr>
<th>E =</th>
<th>Te−Te</th>
<th>Te−Se</th>
<th>Te−S</th>
<th>Se−Se</th>
<th>Se−S</th>
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<td>S</td>
<td>3 (2)</td>
<td>4 (3)</td>
<td>207 (141)</td>
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Table 4: Structural features of less common E−E′−E′′, E···E′−E′′, or E−E′···E′′ trichalcogenides characterized by X-ray diffraction analysis.

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(a) Mean values. (b) The angle values are rounded off to the first decimal digit.
(c) Triselenourea dications with different counterions. (d) d(O···Se).
Σ contact distances shorter than \((\cdots\text{Te} \text{ fragments})\) with respect to the sum of the covalent radii.

\[\text{1,3a,6,6a-tetrahydro-1,6,6a-triselena-4a(\cdots\text{Te} \text{ fragments})}\]

\[\text{with respect to the sum of the covalent radii.}\]

\[\text{1,3a,6,6a-tetrahydro-1,6,6a-triselena-4a(\cdots\text{Te} \text{ fragments})}\]

\[\text{with respect to the sum of the covalent radii.}\]

\[\text{1,3a,6,6a-tetrahydro-1,6,6a-triselena-4a(\cdots\text{Te} \text{ fragments})}\]

\[\text{with respect to the sum of the covalent radii.}\]

\[\text{1,3a,6,6a-tetrahydro-1,6,6a-triselena-4a(\cdots\text{Te} \text{ fragments})}\]

\[\text{with respect to the sum of the covalent radii.}\]

\[\text{1,3a,6,6a-tetrahydro-1,6,6a-triselena-4a(\cdots\text{Te} \text{ fragments})}\]

\[\text{with respect to the sum of the covalent radii.}\]

\[\text{1,3a,6,6a-tetrahydro-1,6,6a-triselena-4a(\cdots\text{Te} \text{ fragments})}\]

\[\text{with respect to the sum of the covalent radii.}\]

\[\text{1,3a,6,6a-tetrahydro-1,6,6a-triselena-4a(\cdots\text{Te} \text{ fragments})}\]

\[\text{with respect to the sum of the covalent radii.}\]

\[\text{1,3a,6,6a-tetrahydro-1,6,6a-triselena-4a(\cdots\text{Te} \text{ fragments})}\]

\[\text{with respect to the sum of the covalent radii.}\]

\[\text{1,3a,6,6a-tetrahydro-1,6,6a-triselena-4a(\cdots\text{Te} \text{ fragments})}\]

\[\text{with respect to the sum of the covalent radii.}\]

\[\text{1,3a,6,6a-tetrahydro-1,6,6a-triselena-4a(\cdots\text{Te} \text{ fragments})}\]

\[\text{with respect to the sum of the covalent radii.}\]
species are S-, Se-, or Te-containing neutral molecules, dicatonic species will be generated having the central atom in a hypervalent state. Among these systems, those having three S=S=S aligned sulphur atoms [265–314] have been found only in the class of the pincer-type molecules, with the central sulphur able to bind or to move apart the terminal ones by oxidation/reduction processes. It is noteworthy to observe that most of the molecules belonging to the E=E′-E pincer-type arrangements and many other trichalcogen systems are fairly symmetric, even if examples of strongly asymmetric situations are also numerous.

Although our discussion is limited to the structural features of linear trichalcogen fragments (various combinations of S, Se, and Te), we have also included in Table 4 the only known example of an organic dichalcogen dication system having a strong contact with an oxygen atom [357, 358]. X-ray analysis of this dication confirmed the linear geometry of the O-Se-Se moiety (165°) and an Se-Se bond (2.39 Å) which, similarly to what found in the above-described Mo and W clusters [257, 335], is only slightly elongated with respect to an Se-Se bond in diselenides (2.34 Å). This compound represents a good example of a hypervalent selenium compound having the two bonds strongly unbalanced (bond orders very far from the value of 0.5 expected for a balanced 3c-4e bond system). For this reason it resembles many other similar systems, such as the adduct of N,N-dimethylimidazoline-2-selone with the pseudo-halogen ICN recently reported by us (see below in the last section); in both cases, one of the bonds tends to be a single bond, while the other bond is very elongated and tends to assume a purely ionic character.

5. DICHALCOGEN-HALIDES

Two chalcogen and one halogen atoms as closed-shell species can be aligned in only two possible ways: the halogen in the terminal (E-E′-X) or in the central (E-X-E′) position. Both arrangements are known and they will be discussed separately.

5.1. E-E′-X fragments

Table 5 shows the number of linear E=E′-X fragments crystallographically characterized from a search of the Cambridge Structural Database, by imposing the linearity of the system (∠E-E′-X angle > 165°) and either the presence of two covalent E-E′ and E′-X bonds or the presence of one E-E′ covalent bond and one E′-X nonbonding contact shorter than ΣrVdW = 0.3 Å.

It is interesting to note that in the case of the S=S-X fragment (X = Cl, Br, I) the number of structures characterized by the presence of a linear S=S· · ·X moiety is considerably higher than that featuring the S=S-X one (17 versus 4). Fragments having fairly covalent bonds have been found exclusively as part of some molybdenum clusters [390, 391, 399, 401, 445–447]. These clusters are very similar to those previously described in the discussion of trichalcogenides species, with the difference that the halide takes the place of the bridging E2- anion. On the basis of their insolubility in water and their solubility in the common organic solvents, the authors concluded that the S-X bonds should be prevalently covalent in character. In fact, their structural features seem to be consistent with the presence of an [S=S-X]3- anion, deriving from the removal of a couple of electrons from the aligned S3- and X- closed-shell species. The sum of the S=S and S-X bond lengths in these fragments is about 23% longer than the sum of the covalent radii and about 31% shorter than the sum of the van der Waals radii, in agreement with a 3c-4e bond model. The scatter plots of d(S=S) versus

---

**Figure 8:** Scatter plot of d1 versus d2 for linear (angle > 165°) Se−Te−Se fragments from a search of the CSD. The symbol (♦) refers to the 39 Se−Te−Se fragments (22 structures) featuring bond distances ranging from ΣrVdW to (ΣrVdW − 0.6); the symbol (●) refers to the 2 Se− · · ·Te−Se fragments (2 structures) featuring Se− · · ·Te contact distances shorter than (ΣrVdW − 0.3). The mean bond lengthening within Se−Te−Se fragments is 11.5% (16.1% on Se− · · ·Te−Se fragments) with respect to the sum of the covalent radii.

**Figure 9:** Scatter plot of d1 versus d2 for linear (angle > 165°) S−Te−S fragments from a search of the CSD. The symbol (♦) refers to the 187 S−Te−S fragments (127 structures) featuring bond distances ranging from ΣrVdW to (ΣrVdW − 0.6); the symbol (●) refers to the 20 S− · · ·Te−S fragments (14 structures) featuring S− · · ·Te contact distances shorter than (ΣrVdW − 0.3). The mean bond lengthening within S−Te−S fragments is 12.6% (21.0% on S− · · · Te−S fragments) with respect to the sum of the covalent radii.
Table 5: Occurrence of linear E−E′−X and E−E′···X fragments crystallographically characterized from a search of the Cambridge Structural Database (number of crystal structures in parentheses). (a)

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<th>S−Te</th>
<th>Se−Se</th>
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<td>35 (26)</td>
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Figure 10: Scatter plot of d(S−S) versus d(S−Cl) for linear (angle > 165°) S−S−Cl fragments from a search of the CSD. The symbol (●) refers to the 10 S−S−Cl fragments (4 structures) featuring bond distances ranging from Σrcov to (ΣrVdW = 0.6); the symbol (○) refers to the 39 S−S···Cl fragments (17 structures) featuring S···Cl contact distances shorter than (ΣrVdW = 0.3). The mean bond lengthening within S−S−Cl fragments is 21.5% (26.1% on S−S···Cl fragments) with respect to the sum of the covalent radii.

Figure 11: Scatter plot of d(S−S) versus d(S−Br) for linear (angle > 165°) S−S−Br fragments from a search of the CSD. The symbol (●) refers to the 2 S−S−Br fragments (1 structure) featuring bond distances ranging from Σrcov to (ΣrVdW = 0.6); the symbol (○) refers to the 45 S−S···Br fragments (16 structures) featuring S···Br contact distances shorter than (ΣrVdW = 0.3). The mean bond lengthening within S−S−Br fragments is 21.1% (23.7% on S−S···Br fragments) with respect to the sum of the covalent radii.

Numerous crystal structures have been reported in the literature that feature linear S−Te−X (X = Cl, Br, I) fragments (references are collected in Table 5). Contrary to what found on searching the CSD for S−S−X fragments, for these linear arrangements, almost all the fragments feature covalent S−Te and Te−X bonds (S−Te−X systems). Only one structure containing an S−Te···Cl [244] moiety has been found by searching for S−Te···X systems [Σrcov = 0.6 < d(T···X) < (ΣrVdW = 0.3)]. As shown in Figures 13, 14, and 15, for these three series of compounds the two bonds are strictly correlated in wide ranges of variability.

The sum of S−Te and Te−X bond distances within these three-body systems is 10.8%, 11.6%, and 7.3% longer than the sum of the covalent radii for X = Cl, Br, and I, respectively, in good agreement with the hypervalent nature of the central tellurium atom. The other mixed dichalcogen fragments bonded to a halide, characterized by X-ray diffraction, are very few and they are collected in Table 6.
Table 6: Structural features of the less common $E-E'-X$ and $E-E'\cdots X$ ($E, E' = S, Se, X = \text{halogen}$) linear three-body systems and of some selected $E-E'-X$ ($E = S, Se, E' = Te, X = \text{halogen}$) fragments.

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<td>167.8</td>
<td>[437]</td>
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</table>

$^5$The angle values are rounded off to the first decimal. *Mean values.
Figure 12: Scatter plot of $d(S-S)$ versus $d(S-I)$ for linear (angle $> 165^\circ$) $S-S-I$ fragments from a search of the CSD. The symbol (♦) refers to the 7 $S-S-I$ fragments (4 structures) featuring bond distances ranging from $\Sigma_{\text{cov}}$ to $(\Sigma_{\text{vdW}} = 0.6)$; the symbol (♦) refers to the 25 $S-S-I$ fragments (11 structures) featuring $S-I$ contact distances shorter than $(\Sigma_{\text{vdW}} = 0.3)$. The mean bond lengthening within $S-S-I$ fragments is 19.2% (21.5% on $S-S-I$ fragments) with respect to the sum of the covalent radii.

Figure 13: Scatter plot of $d(S-Te)$ versus $d(Te-Cl)$ for linear (angle $> 165^\circ$) $S-Te-Cl$ fragments from a search of the CSD. The symbol (♦) refers to the 52 $S-Te-Cl$ fragments (38 structures) featuring bond distances ranging from $\Sigma_{\text{cov}}$ to $(\Sigma_{\text{vdW}} = 0.6)$; the symbol (♦) refers to the 1 $S-Te-Cl$ fragment (1 structure) featuring $Te-Cl$ contact distances shorter than $(\Sigma_{\text{vdW}} = 0.3)$. The mean bond lengthening within $S-Te-Cl$ fragments is 10.8% (24.5% on $S-Te-Cl$ fragment) with respect to the sum of the covalent radii.

Figure 14: Scatter plot of $d(S-Te)$ versus $d(Te-Br)$ for the 52 linear (angle $> 165^\circ$) $S-Te-Br$ fragments (38 structures) featuring bond distances ranging from $\Sigma_{\text{cov}}$ to $(\Sigma_{\text{vdW}} = 0.6)$ from a search of the CSD. The mean bond lengthening within $S-Te-Br$ fragments is 11.6% with respect to the sum of the covalent radii.

Figure 15: Scatter plot of $d(S-Te)$ versus $d(Te-I)$ for the 20 linear (angle $> 165^\circ$) $S-Te-I$ fragments (19 structures) featuring bond distances ranging from $\Sigma_{\text{cov}}$ to $(\Sigma_{\text{vdW}} = 0.6)$ from a search of the CSD. The mean bond lengthening within $S-Te-I$ fragments is 7.3% with respect to the sum of the covalent radii.

Differently from $S-S-X$, the $S-Se-X$ fragments have been found in some dimeric structures with bridging halides [383, 386]. Also in these cases the sum of the $S-Se$ and $Se-X$ bond lengths shows elongation ($\sim 19\%$) with respect to the sum of the covalent radii, and shortening ($\sim 30\%$) with respect to the sum of the van der Waals radii. A certain number of structures characterized by the linear $Se-Te-X$ system have also been found. It is noteworthy that the $S-Te$ and $Se-Te$ bonds get shortened as the $Te-X$ bond becomes more ionic (on changing $X$ from I to Br and to Cl, see the examples reported in Table 7), their bond orders approaching the value of 1.

In the case of the chloroderivatives $E-Te\cdots Cl$ ($E = S, Se$, Table 7), the $S-Te$ and $Se-Te$ bonds are only 0.077 Å and 0.080 Å longer than the sum of the covalent radii, making the structural features of these compounds similar to those of the fragments $Se-Te\cdots O$ [358] and $NC-Se\cdots I$ (see below in the last section). Finally, five structures containing the linear $Te-Te-I$ arrangement have been reported in the literature; two of them [437] are inserted in molybdenum clusters in a fashion similar to that found for the $S-S-X$ and $Se-Se-X$ groups, two are arranged to form $(Ph-Te-I)_4$
tetramers [435, 436] and only one, \((\text{Mes})_2\text{Te} \rightarrow \text{Te} \rightarrow \text{Te} \rightarrow \text{Te} \rightarrow \text{I})\), can be considered as derived from the three aligned closed-shell \(\text{Mes}_3\text{Te}\), \(\text{Mes}\text{Te}^\text{−}\), and \(\text{I}^\text{−}\) species, by the removal of a couple of electrons. The analysis of the structural features of all these fragments is consistent with their description as three-body systems, the central Te atom being hypervalent.

### 5.2. E−X−E’ fragments

Table 8 collects the structural features of all the linear \(E\rightarrow X\rightarrow E’\) (\(E, E’ = \text{chalcogen atom}; X = \text{halogen}\)) fragments found by searching the Cambridge Structural Database.

Systems of this type have been found with the three halogens (Cl, Br, and I), and all the fragments have the same chalcogen (\(E = E’\)) atom at the two sides of the halogen; no mixed species (\(E \neq E’\)) have been reported until now. Moreover, from the data in Table 8 it is interesting to note that with the exception of RIWDUW [473] which is polymeric and shows three different couples of fairly asymmetric Te–Cl bonds, all the other compounds feature the two chalcogen atoms bound to the central halogen in symmetric or only slightly asymmetric fashion, and most of the angles are very close to 180°. In all cases, the shortening of the E–X bond with respect to the sum of the covalent radii (the mean S–I bond length calculated from the structural data of all six compounds characterized by the S–I–S group is elongated of about 17%), the shortening with respect to the van der Waals radii (the mean S–I bond length is shortened by ∼30%) and the linearity of the systems are consistent with the hypervalency of the central atom.

### 6. CHALCOGEN-DIHALIDES

Analogously to dichalcogen-halides, there are only two possibilities to build chalcogen-dihalides moieties: the chalcogen can be in the terminal (\(E\rightarrow X\rightarrow Y\)) or in the central (\(X\rightarrow E\rightarrow Y\)) position. These two arrangements correspond to the well-known CT and “T-shaped” adducts between chalco-

gen donors and dihalogens, respectively, and will be discussed separately.

#### 6.1. E−X−Y fragments

For a more detailed discussion on this class of compounds the reader is referred to the review by Lippolis and Isaia [474]. The number of linear \(E\rightarrow X\rightarrow Y\) CT fragments crystallographically characterized from a search on the Cambridge Structural Database is reported in Table 9.

As one can see most of the adducts are obtained between sulphur donors (\(D\)) and diiodine, on the contrary, no compounds of this type are known with Te donors (the only reported structures featuring a \(\text{Te} \rightarrow \text{I} \rightarrow \text{I}\) arrangement are characterized by long \(\text{I} \cdots \text{I}\) contacts). The \(\sigma^\text{−}\rightarrow \sigma^\text{∗}(\text{XY})\) charge-transfer model accounts very well for the chemical bond in these \(E\rightarrow X\rightarrow Y\) systems. Scheme 2 can be easily adapted to any type of donor/acceptor couple [with the substitutions of \(np\) with \(\sigma(D)\) and \(\sigma^\text{∗}(X)\) with \(\sigma^\text{∗}(XY)\)], bearing in mind that each couple will have a proper match of energy between the interacting orbitals. We will focus our attention on the adducts between sulfur donors and I\(_2\), since for them it is possible to fine tune the lone pair energy of the donor atom by changing its chemical surrounding; therefore any type of adduct from very weak to extremely strong can be obtained. In the case of very weak interactions, each fragment holds its identity with a small reciprocal perturbation; the effect of such perturbation on the halogen molecule consists in the lowering to some extent of its bond order. In terms of the simplified MO diagram reported in Scheme 2, weak adducts correspond to a poor energy match between the interacting \(\sigma(D)\) and \(\sigma^\text{∗}(I_2)\) MO orbitals. Most of adducts between sulfur compounds and I\(_2\) belong to the class of weak adducts. Since the stabilization of the adduct only depends on the in-phase combination of the interacting orbitals, which is bonding between the donor atom and the central iodine, and antibonding between the two iodine atoms, the two bond lengths are strictly correlated and a shortening in the \(D \cdots I\) bond distance is accompanied by a lengthening in the \(I \cdots I\) one. Without doubt, such types of adducts must be considered two-coordinate hypervalent compounds of iodine, like \(I_3^\text{−}\). However, there is a substantial difference between an \(I_3^\text{−}\) and a \(D \cdots I\) system; while in the case of \(I_3^\text{−}\) the introduction of an asymmetry, by increasing removal of one terminal iodine as \(I^\text{−}\), generates in the limit case a strongly asymmetric \(I \cdots I \cdots I\) system, in the case of the charge-transfer adducts, two different asymmetric systems can be generated depending on which bond, \(D \cdots I\) or \(I \cdots I\), is the weakest one. They correspond to two different charge-transfer adducts: \(\sigma(D)\rightarrow \sigma^\text{∗}(I)\) and \(\sigma(I^\text{−})\rightarrow \sigma^\text{∗}(1–D)\). It is possible to pass almost continuously from a balanced situation with the two bonds having a bond order value of about 0.5 [10–I-2 “hypervalent system” for analogy to \(I_3^\text{−}\)], to the two different limit cases in which one bond assumes an increasingly ionic character. Consequently, also these limit cases featuring a strong asymmetry between the two bonds must be included among the 10-I-2 hypervalent compounds \(D \cdots I^\text{−} \cdots I\) and \(D \cdots I \cdots I\).

---

**Table 7**: Examples of the shortening of the \(S\rightarrow Te\) and \(Se\rightarrow Te\) bonds on passing from I to Br and to Cl derivatives.

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<td></td>
<td></td>
<td>2.480 [377]</td>
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</tr>
<tr>
<td></td>
<td>Br</td>
<td>2.468 [377]</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>2.476 [317]</td>
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</tr>
<tr>
<td></td>
<td>I</td>
<td>2.521 [317]</td>
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**R=PSe–Te–X**

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</tr>
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<td></td>
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<td>2.906 [439]</td>
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*\(R = \text{morpholino for } X = \text{Cl and Br}; R = \text{butyl for } X = \text{I}\).*
Table 8: Structural features of all the dichalcogen-halogen (E−X−E') fragments determined by X-ray diffraction analysis (the E−X···E' fragments have not been reported).

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<th>E'</th>
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<th>d(X−E') (Å)</th>
<th>θ E−X−E' (°)</th>
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<td>Te</td>
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<td>2.988*</td>
<td>172.3*</td>
<td>[473]</td>
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5 The angle values are rounded off to the first decimal. * Mean values. ** The Se−Br−Se arrangement is part of the BrI₄Se₂⁺ anion.
6 Polymeric structure. *The Se−Cl−Se arrangement is part of the SeCl₅⁻ anion.

The scatter plot of d(S−I) versus d(I−I) relative to all the reported adducts between sulphur donors and diiodine is reported in Figure 16.

Apart for some dispersion of the data, which was also found for the other examined three-body systems, it clearly appears that the two bond lengths are strictly correlated in a wide range of values. A similar correlation has been found in the case of adducts of selenium donors with diiodine (Figure 17) and sulfur donors with Br (Figure 18), well represented in the literature. Due to the paucity of experimental data, no correlation is evident in the analogous scatter plots for the linear adducts of chalcogen donors with the other dihalogen/interhalogens molecules, including the case of d(Te−I) versus d(I···I). The structural features of less common linear adducts between chalcogen donors and dihalogen/interhalogens molecules are collected in Table 10.

62. X−E−Y fragments

This arrangement corresponds to the well-known “T-shaped” adducts between chalcogen-donors and dihalogens. The numbers of linear X−E−Y fragments crystallographically characterized and found by searching the Cambridge Structural Database are reported in Table 11.

While all the dihalogens/interhalogens combinations with selenium and tellurium have been reported in the literature, only few X−S−X moieties (X = Cl,Br) and no X−S−Y (X ≠ Y = halogen atoms) arrangements with sulphur as central atom are known. Indeed, sulphur donors show a preference to form linear charge-transfer type arrangement with the halogens (Table 9), absolutely unknown for the tellurium donors. Since several types of linear X−E−Y fragments are very numerous, the corresponding structural data

7 A peculiar case is represented by a byproduct of the reaction between the neutral dithiolene [Pd(Et₂timdt)₂] (Et₂timdt = formally monoreduced diethylimidazolidine-2,4,5-trithione) and an excess of bromine, [(Et₂timdt)Br]₂⁺(Br₂)(⋅(Br₂)₃), containing two [L−S−Br]⁺ thione-bromosulfanyl cations [475]. We described this compound as anionic couples formed by the organic framework bearing a double positive charge and the two terminal S−Br bonds, and the two Br⁻ ions which are positioned next to the sulfur atoms to afford two very asymmetric linear Br−S−⋯Br moieties. The strong asymmetry is determined by several contacts between the Br⁻ and Br₂ molecules. Thus, each Br⁻ lies in a pseudo-octahedral environment determined by four Br₂ molecules and two S−Br groups all acting as acceptors of the Br⁻ electron density. It is interesting to note that the Br₂ molecules are so firmly held in the crystal that after one year at room temperature and at air the crystals were unchanged without loss of bromine. The great stability of the Br₂ molecules within the crystal lattice can be explained in terms of donor/acceptor interaction between Br⁻ and six π* orbitals of the Br₂ molecule. The π* orbitals of each Br₂ molecule are delocalized. The Br⁻ and Br₂ molecules form a nearly linear Br−S−Br+-Br⁻ bite angle, where the halogen molecules interact each other at 90° through a π*(X₂) → σ*(X₂) donation (X = Br, I).
Table 9: Occurrence of linear E−X−Y CT fragments crystallographically characterized from a search of the Cambridge Structural Database (number of crystal structures in parentheses).

<table>
<thead>
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<th>E</th>
<th>Te</th>
<th>Se</th>
<th>S</th>
</tr>
</thead>
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<td>I</td>
<td>9 (9)</td>
<td>32 (24)</td>
<td>120 (85)</td>
</tr>
<tr>
<td>I</td>
<td>Br</td>
<td>—</td>
<td>5 (5)</td>
<td>13 (11)</td>
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<tr>
<td>I</td>
<td>Cl</td>
<td>—</td>
<td>3 (3)</td>
<td>4 (4)</td>
</tr>
<tr>
<td>Br</td>
<td>Br</td>
<td>3 (3)</td>
<td>8 (6)</td>
<td>9 (9)</td>
</tr>
<tr>
<td>Br</td>
<td>Cl</td>
<td>—</td>
<td>—</td>
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</tr>
<tr>
<td>Cl</td>
<td>Cl</td>
<td>3 (3)</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

(a) Only contacts. References [476–483].
(b) References [42, 444, 466, 484–498].
(c) References [47, 69, 108, 464, 474, 490, 493, 496, 499–549].
(d) References [30, 42, 148].
(e) References [25, 47, 69, 510, 550–554].
(f) References [148, 555, 556].
(g) References [510, 553–555].
(h) Only contacts. References [480, 557, 558].
(i) Only the structure of [559] is a CT adduct. References [50, 559–561].
(j) Only two structures are of the CT type. References [45, 63, 475, 532, 562–564].
(k) Only contacts. References [360, 483, 565].

![Figure 16: Scatter plot of d(S−I) versus d(I−I) for linear (angle > 165°) S−I−I fragments from a search of the CSD. The symbol (♦) refers to the 67 S−I−I fragments (50 structures) featuring bond distances ranging from Σrcov to (ΣrVdW − 0.6); the symbol (◦) refers to the 50 S−I−I fragments (38 structures) featuring S−I contact distances shorter than (ΣrVdW − 0.3); the symbol (●) refers to the 3 S−I−I fragments (3 structures) featuring I−I contact distances shorter than (ΣrVdW − 0.3). The mean bond lengthening within S−I−I fragments is 12.2% (19.2% on S−I−I, and 14.1% on S−I−I fragments, resp.) with respect to the sum of the covalent radii.](image1)

![Figure 17: Scatter plot of d(Se−I) versus d(I−I) for linear (angle > 165°) Se−I−I fragments from a search of the CSD. The symbol (♦) refers to the 16 Se−I−I fragments (12 structures) featuring bond distances ranging from Σrcov to (ΣrVdW − 0.6); the symbol (◦) refers to the 10 Se−I−I fragments (5 structures) featuring Se−I contact distances shorter than (ΣrVdW − 0.3); the symbol (●) refers to the 6 Se−I−I fragments (6 structures) featuring I−I contact distances shorter than (ΣrVdW − 0.3). The mean bond lengthening within Se−I−I fragments is 10.5% (12.4% on Se−I−I, and 14.4% on Se−I−I fragments, resp.) with respect to the sum of the covalent radii.](image2)

![Figure 18: Scatter plot of d(1−Br) versus d(S−I) for the 13 linear (angle > 165°) S−I−Br fragments (11 structures) featuring bond distances ranging from Σrcov to (ΣrVdW − 0.6) from a search of the CSD. The mean bond lengthening within S−I−Br fragments is 10.5% with respect to the sum of the covalent radii.](image3)

are given as scatter plots of the two X−E and E−Y bond lengths (Figures 19, 20, 21, 22, and 23).

As one can see, there is a high dispersion of points in the scatter plots; however, in all the analyzed three-body systems the two bond lengths can be considered correlated and both strongly asymmetric and symmetric fragments can be found.

In Table 12, the structural features of less common X−E−Y fragments are reported; there are six examples of hypervalent chalcogen atoms bonded to two different halogen atoms, and, as already said, none of them features a central sulphur atom. It is interesting to note that in such systems the bond between the chalcogen and the lighter halogen is much more elongated with respect to the sum of the covalent radii (more ionic bond) than that involving the heavier halogen. In SUSMIC and in IDAZUI, Se−Cl and Se−Br are even longer than Se−Br and Se−I, respectively.
Table 10: Structural features of less common $E$–$X$–$Y$ linear chalcogenihalides of the CT type, characterized by X-ray diffraction analysis.

<table>
<thead>
<tr>
<th>Compound reference code</th>
<th>$E$</th>
<th>$X$</th>
<th>$Y$</th>
<th>$E$–$X$ (Å)</th>
<th>$X$–$Y$ (Å)</th>
<th>$\angle E$–$X$–$Y$ (°)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>HAMCII</td>
<td>S</td>
<td>I</td>
<td>Cl</td>
<td>2.534</td>
<td>2.761</td>
<td>176.4</td>
<td>[510]</td>
</tr>
<tr>
<td>LIFIXH</td>
<td>S</td>
<td>I</td>
<td>Cl</td>
<td>2.556</td>
<td>2.604</td>
<td>179.9</td>
<td>[555]</td>
</tr>
<tr>
<td>NAHQIX</td>
<td>S</td>
<td>I</td>
<td>Cl</td>
<td>2.575</td>
<td>2.558</td>
<td>176.1</td>
<td>[553]</td>
</tr>
<tr>
<td>SIBJOC</td>
<td>S</td>
<td>I</td>
<td>Cl</td>
<td>2.614</td>
<td>2.586</td>
<td>174.9</td>
<td>[554]</td>
</tr>
<tr>
<td>RORNIV(b)</td>
<td>S</td>
<td>Br</td>
<td>Br</td>
<td>2.299</td>
<td>2.717</td>
<td>175.0</td>
<td>[562]</td>
</tr>
<tr>
<td>RORNIV01(b)</td>
<td>S</td>
<td>Br</td>
<td>Br</td>
<td>2.328</td>
<td>2.705</td>
<td>176.0</td>
<td>[63]</td>
</tr>
<tr>
<td>IRABEI(c)</td>
<td>Se</td>
<td>Br</td>
<td>Br</td>
<td>2.645</td>
<td>2.358</td>
<td>174.2</td>
<td>[559]</td>
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<td>LIGFIQ</td>
<td>Se</td>
<td>I</td>
<td>Cl</td>
<td>2.625</td>
<td>2.690</td>
<td>178.9</td>
<td>[148]</td>
</tr>
<tr>
<td>LIGFIQ01</td>
<td>Se</td>
<td>I</td>
<td>Cl</td>
<td>2.618</td>
<td>2.690</td>
<td>178.7</td>
<td>[148]</td>
</tr>
<tr>
<td>OXSEIC</td>
<td>Se</td>
<td>I</td>
<td>Cl</td>
<td>2.630</td>
<td>2.731</td>
<td>175.8</td>
<td>[556]</td>
</tr>
<tr>
<td>NOWLOA</td>
<td>Se</td>
<td>I</td>
<td>Br</td>
<td>2.808</td>
<td>2.641</td>
<td>177.3</td>
<td>[30]</td>
</tr>
<tr>
<td>NOWLUG</td>
<td>Se</td>
<td>I</td>
<td>Br</td>
<td>2.664</td>
<td>2.797</td>
<td>175.8</td>
<td>[30]</td>
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<tr>
<td>WIPPAM</td>
<td>Se</td>
<td>I</td>
<td>Br</td>
<td>2.636</td>
<td>2.813</td>
<td>177.1</td>
<td>[148]</td>
</tr>
<tr>
<td>YEYFIR</td>
<td>Se</td>
<td>I</td>
<td>Br</td>
<td>2.689</td>
<td>2.908</td>
<td>176.9</td>
<td>[42]</td>
</tr>
</tbody>
</table>

(a) The angle values are rounded off to the first decimal. (b) Polymorphs. (c) This is the unique example of CT type adduct between a selenium donor with bromine: the formation of a Br–Se–Br group determines very favorable electronic and steric effects to prevent the formation of the same arrangement on the second selenium atom and to promote the CT type adduct. It must be noted that the Se···Br interaction is enough weak to determine a lengthening of the Br–Br bond of only 0.078 Å.

Table 11: Occurrence of linear $X$–$E$–$Y$ fragments crystallographically characterized from a search of the Cambridge Structural Database.

<table>
<thead>
<tr>
<th>$X$</th>
<th>$Y$</th>
<th>$E$</th>
<th>Te</th>
<th>Se</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td>Cl</td>
<td>194(a)</td>
<td>53(b)</td>
<td>4(c)</td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>Br</td>
<td>1(d)</td>
<td>2(e)</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>I</td>
<td>1(f)</td>
<td>—</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>Br</td>
<td>Br</td>
<td>84(g)</td>
<td>63(h)</td>
<td>3(i)</td>
<td></td>
</tr>
<tr>
<td>Br</td>
<td>I</td>
<td>1(j)</td>
<td>1(k)</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>I</td>
<td>I</td>
<td>71(l)</td>
<td>4(m)</td>
<td>—</td>
<td></td>
</tr>
</tbody>
</table>


7. CHALCOGEN ∙ XCN (X = HALOGEN) ADDUCTS

As reported before, we wish also to consider in this discussion “T-shaped” adducts obtained from the reaction between chalcogen donors and pseudo-halogen X–CN (X = Cl, Br and I). Some compounds characterized by X-ray diffraction analysis and featuring X–E–CN moieties (X = halogen, E = chalcogen) are collected in Table 13.

The compound CYMIMB, reported by Arduengo and Burgess [800], has been included in the table for its strict similarity with EZUZII, reported by us [832]. Both compounds have a “T-shaped” arrangement around the chalcogen atom and are characterized by very different E–X and E–CN bond lengths; the chalcogen–carbon bond is only slightly elongated with respect to the sum of covalent radii (bond order close to 1) and the chalcogen-halogen bond is close to be a completely ionic bond. These compounds closely resemble many asymmetric systems above described and in particular the pincer-type molecule bearing the O···Se–Se group (Table 4). The closeness of the chalcogen–CN and the Se–Se bond distances to the corresponding single bonds, respectively, and the long chalcogen-halogen and selenium-oxygen distances, strongly support the analogy between these two classes of compounds. According to the 3c-4e model, the different energy levels of the three combined p orbitals (there is a good overlap between the orbitals from E and C due to a good match of their energies) produce a bonding MO having a small contribution of the p orbital of the halogen, which vice versa mainly contributes to the nonbonding orbital, thus carrying most of the negative charge. In terms of the charge-transfer model, all the compounds of this type can be properly described as originated by a very weak donation from one halide orbital to the E–CN antibonding orbital (e.g., no (I−) → σ*(E–CN)); the weak interaction has the consequence of a small lengthening in the E–CN bond distance, exactly as verified in numerous adducts between weak S donors and diiodine.
Table 12: Structural features of the less common X−E−Y linear chalcogendihalides characterized by X-ray diffraction analysis.

<table>
<thead>
<tr>
<th>Compound reference code</th>
<th>X</th>
<th>E</th>
<th>Y</th>
<th>d( X−E ) (Å)</th>
<th>d( E−Y ) (Å)</th>
<th>∠ X−E−Y(*)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>CFMBXT</td>
<td>Cl</td>
<td>S</td>
<td>Cl</td>
<td>2.126</td>
<td>2.552</td>
<td>167.6</td>
<td>[730]</td>
</tr>
<tr>
<td>CLPHSC10</td>
<td>Cl</td>
<td>S</td>
<td>Cl</td>
<td>2.256</td>
<td>2.322</td>
<td>174.9</td>
<td>[731]</td>
</tr>
<tr>
<td>TOSXII</td>
<td>Cl</td>
<td>S</td>
<td>Cl</td>
<td>2.341</td>
<td>2.384</td>
<td>166.3</td>
<td>[732]</td>
</tr>
<tr>
<td>TOSXOO</td>
<td>Cl</td>
<td>S</td>
<td>Cl</td>
<td>2.295</td>
<td>2.365</td>
<td>175.9</td>
<td>[732]</td>
</tr>
<tr>
<td>BIMMAL</td>
<td>Br</td>
<td>S</td>
<td>Br</td>
<td>2.437</td>
<td>2.495</td>
<td>171.6</td>
<td>[47]</td>
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<tr>
<td>MIMZDB</td>
<td>Br</td>
<td>S</td>
<td>Br</td>
<td>2.451</td>
<td>2.538</td>
<td>176.9</td>
<td>[800]</td>
</tr>
<tr>
<td>OBUQEHE</td>
<td>Br</td>
<td>S</td>
<td>Br</td>
<td>2.493</td>
<td>2.493</td>
<td>179.4</td>
<td>[788]</td>
</tr>
<tr>
<td>SUSMIC</td>
<td>Cl</td>
<td>Se</td>
<td>Br</td>
<td>2.802(b)</td>
<td>2.412(b)</td>
<td>173.3(b)</td>
<td>[730]</td>
</tr>
<tr>
<td>SUSNAV</td>
<td>Cl</td>
<td>Se</td>
<td>Br</td>
<td>2.466</td>
<td>2.571</td>
<td>176.2</td>
<td>[793]</td>
</tr>
<tr>
<td>IDAZUI(c)</td>
<td>Br</td>
<td>Se</td>
<td>I</td>
<td>2.831(b)</td>
<td>2.618(b)</td>
<td>174.6(b)</td>
<td>[802]</td>
</tr>
<tr>
<td>GEPPUM</td>
<td>I</td>
<td>Se</td>
<td>I</td>
<td>2.756</td>
<td>2.850</td>
<td>176.3</td>
<td>[486]</td>
</tr>
<tr>
<td>HELDUX</td>
<td>I</td>
<td>Se</td>
<td>I</td>
<td>2.768</td>
<td>2.854</td>
<td>175.4</td>
<td>[830]</td>
</tr>
<tr>
<td>ZOBDID</td>
<td>I</td>
<td>Se</td>
<td>I</td>
<td>2.738</td>
<td>2.886</td>
<td>178.6</td>
<td>[498]</td>
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<td>ZOBDUP</td>
<td>I</td>
<td>Se</td>
<td>I</td>
<td>2.743</td>
<td>2.900</td>
<td>177.5</td>
<td>[498]</td>
</tr>
<tr>
<td>XAGVIK</td>
<td>Cl</td>
<td>Te</td>
<td>Br</td>
<td>2.659</td>
<td>2.577</td>
<td>169.9</td>
<td>[733]</td>
</tr>
<tr>
<td>CEFREX</td>
<td>Br</td>
<td>Te</td>
<td>I</td>
<td>2.868</td>
<td>2.903</td>
<td>177.9</td>
<td>[580]</td>
</tr>
</tbody>
</table>

(a) The angle values are rounded off to the first decimal. (b) Mean values. (c) This compound is the unique example of Se-hypervalent compound with IBr. Note that the mean value of the Se−I bond length is shorter than the Se−Br one.

Table 13: Structural features of all the T-shaped compounds containing the X···E−CN fragment (E = chalcogen; X = halogen) from a search of the Cambridge Structural Database.

<table>
<thead>
<tr>
<th>Compound reference code</th>
<th>X</th>
<th>E</th>
<th>X···E (Å)</th>
<th>E−CN (Å)</th>
<th>∠ X···E−Y(*)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>BOJPUL</td>
<td>Cl</td>
<td>Te</td>
<td>2.924</td>
<td>2.140</td>
<td>167.9</td>
<td>[831]</td>
</tr>
<tr>
<td>BOJRAP</td>
<td>Br</td>
<td>Te</td>
<td>3.100</td>
<td>2.131</td>
<td>167.6</td>
<td>[831]</td>
</tr>
<tr>
<td>BOJREX</td>
<td>I</td>
<td>Te</td>
<td>3.299</td>
<td>2.143</td>
<td>170.9</td>
<td>[831]</td>
</tr>
<tr>
<td>CYMIMB(a)</td>
<td>Br</td>
<td>S</td>
<td>3.588(a)</td>
<td>1.757</td>
<td>159.8</td>
<td>[800]</td>
</tr>
<tr>
<td>EZUZII</td>
<td>I</td>
<td>Se</td>
<td>3.300</td>
<td>1.885</td>
<td>174.8</td>
<td>[832]</td>
</tr>
</tbody>
</table>

(a) This compound has not been found searching the Cambridge Structural Database, but has been included in the table for the strict similarity with EZUZII. In CYMIMB, the shorter S···Br distance (3.270 Å) is that of the bromide in trans position with respect to the pentaatomic ring of the donor and not to the CN group.

Figure 19: Scatter plot of $d_1$ versus $d_2$ of the 113 linear (angle > 165°) I−Te−I fragments (71 structures) featuring bond distances ranging from $\Sigma r_{covalent}$ to $(\Sigma r_{vdW} - 0.6)$ from a search of the CSD. The mean bond lengthening within I−Te−I fragments is 9.3% with respect to the sum of the covalent radii.

Figure 20: Scatter plot of $d_1$ versus $d_2$ of the 170 linear (angle > 165°) Br−Te−Br fragments (84 structures) featuring bond distances ranging from $\Sigma r_{covalent}$ to $(\Sigma r_{vdW} - 0.6)$ from a search of the CSD. The mean bond lengthening within Br−Te−Br fragments is 8.1% with respect to the sum of the covalent radii.
Figure 21: Scatter plot of $d_1$ versus $d_2$ for the 405 linear (angle $> 165^\circ$) Cl–Se–Cl fragments (174 structures) featuring bond distances ranging from $\Sigma_{\text{rcov}}$ to ($\Sigma_{\text{VdW}} = 0.6$) from a search of the CSD. The mean bond lengthening within Cl–Te–Cl fragments is 8.0% with respect to the sum of the covalent radii.

Figure 23: Scatter plot of $d_1$ versus $d_2$ for the 130 linear (angle $> 165^\circ$) Cl–Se–Cl fragments (51 structures) featuring bond distances ranging from $\Sigma_{\text{rcov}}$ to ($\Sigma_{\text{VdW}} = 0.6$) from a search of the CSD. The mean bond lengthening within Cl–Se–Cl fragments is 13.8% with respect to the sum of the covalent radii.

**Figure 22:** Scatter plot of $d_1$ versus $d_2$ for the 141 linear (angle $> 165^\circ$) Br–Se–Br fragments (63 structures) featuring bond distances ranging from $\Sigma_{\text{rcov}}$ to ($\Sigma_{\text{VdW}} = 0.6$) from a search of the CSD. The mean bond lengthening within Br–Se–Br fragments is 12.9% with respect to the sum of the covalent radii.

8. CONCLUSION

On the basis of this overview on the structural features of linear three-body systems, involving 16th and 17th group elements, the following conclusions can be drawn.

(i) The Rundle-Pimentel model for electron-rich 3-centre 4-electron systems and the charge-transfer model represent two different approaches able to account for the structural features of these linear three-body systems.

(ii) The Rundle-Pimentel model can be adapted to any set of three aligned atoms, positioning the combining orbitals at the appropriate levels of energy.

(iii) Since three aligned closed-shell atoms can find stabilization only if two electrons are removed from the system, ideally any type of sequence of atoms could be obtained.

(iv) The variability of starting molecules is reflected in the great variety of obtainable structural archetypes. Since a starting molecule can be also a species containing a hypervalent atom, its alignment with other closed-shell species produces molecules in which two or three orthogonal 3c-4e systems are simultaneous present. This is for example the case of anions such as Ph–SeBr$_4^-$ or SeBr$_6^{2-}$.

(v) The Rundle-Pimentel model very well accounts for the 0.5 bond order in symmetric three-body systems since only the lowest MO contributes to the bond formation. In addition, the Rundle-Pimentel model elegantly explains why the two terminal atoms carry more negative charge (or less positive charge for positively charged systems) even in the cases of three identical atoms [such as I$_3^-$ or E(R$_2^2$)–E(R$_2^2$)–E(R$_2^2$)$^{2+}$ dications].

(vi) In these three-body systems, the energy match between the $p$ orbital of the central atom and those of the terminal ones influences the polarization of the formed bonds. This is very important for systems having different terminal atoms: each $p$ orbital will contribute differently to the three molecular orbitals with the consequence of an increased unbalance of the two bonds as the electronegativity difference between the involved elements increases. In such cases, the bond orders of the two bonds diverge from the value of 0.5, one approaching the value of 1 and the other that of 0.

(vii) The strict analogy among all these systems, including the strongly asymmetric ones as the “T-shaped” adduct between the N,N’-dimethyldiazole-2-selone and ICN, supports the hypervalent nature of the selenium atom in this compound in spite of the fact that the bond orders of the two bonds are very different.
(viii) The charge-transfer model explains very well all the very asymmetric systems since this model corresponds to the interaction of two stable fragments (as a dihalogen molecule with a halide, or as chalcogen donor with a dichalcogen dication).

(ix) The energy match between the interacting orbitals of the two fragments (such as a hybrid orbital of the donor and the σ* antibonding molecular orbital of the acceptor) determines the entity of the interaction.

(x) In the CT model, the bond order of 0.5 for the two bonds is reached when the interacting orbitals are at the same level of energy. This corresponds to the introduction of 1 electron on the σ* MO of the acceptor, with the consequent reduction of the bond order from 1 to 0.5.

(xi) An aspect to be emphasized is the fact that in all the structures of these families of compounds, including the very asymmetric systems, the three-body system is always linear, with angles generally larger than 170°. The directionality of the bond is maintained also in presence of strongly unbalanced bonds indicating a valuable contribution of covalence, due to the nδ donoņo − σ* acceptor charge-transfer interaction and supporting the hypervalent character of the central chalcogen atom, independently on the entity of the asymmetry.

(xii) Finally, it is interesting to observe that with only few exception, the systems having different terminal atoms (see, e.g., trihalides X−Z−Y with X ≠ Y or trichalcogenides E−E′−E′′ with E ≠ E′) are less common than the symmetric ones.

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