1. Introduction

The understanding of the atomic interactions involved in crystal structures is fundamental in the crystal engineering field. In a first instance, this knowledge can be correlated with the crystal properties and, in a second instance, it can be applied to the design of crystalline materials for specific applications.

In molecular crystals, the crystal cohesion is attributed to weak attractive forces, unlike strong covalent interactions that hold the atoms bonded in a molecule. Some of these weak interactions, for example the hydrogen bonds between electronegative atoms, have been recognized and studied for a long time (Pimentel & McClellan, 1960; Jeffrey & Saenger, 1991; Steiner, 2002). Nonconventional and weaker hydrogen bonds between AH (AH = OH, NH, etc.) and soft bases (π systems) or between CH and B (B = O, N, etc.), π···π interactions, halogen bonds, cation···π interactions, have become the focus of interest in the last decades due to their potential role in supramolecular chemistry and in biochemical processes (Desiraju & Steiner, 2001; Metrangolo et al., 2008; Nishio et al., 2009; Schneider, 2009; Salonen et al., 2011).

Soft interactions between heavy p-block elements and electronegative atoms are frequent and have been shown to play a significant role in supramolecular chemistry. Tellurium is a chemical element showing this kind of soft interactions, also known as secondary bonding (Alcock, 1972). Organotellurium compounds have been investigated mainly in organic synthesis (Singh & Sharma, 2000; Petragnani & Stefani, 2005), but also in medicine (Ba et al., 2010), in materials science (Steigerwald & Sprinkle, 1987; Hails et al., 2001) and recently in polymerization processes (organotellurium-mediated living radical polymerization (TERP)) (Kitayama et al., 2010) and to protect materials (lubricants, polymers) from oxidation (Shanks et al., 2006).

The type of the Te···X interaction (and the secondary bonding interaction) and its relevance in the tellurium coordination polyhedra have been discussed (Alcock, 1972; Zukerman-Schpector & Haiduc, 2001). This chapter deals with the weak Te···halogen (Te···X) interactions found in organotellurium crystal structures and with the supramolecular...
arrangements derived from them. Some supramolecular self-assemblies based on Te···halogen secondary bonds have been described (Haiduc & Zukerman-Schpector, 2001; Zukerman-Schpector et al., 2002; Srivastava et al., 2004; Cozzolino et al., 2011). This chapter presents a systematic update including quantitative aspects. It is performed an analysis of the influence of several factors on the type of supramolecular pattern such as the polymorphism or the nature of halogen.

2. The Te···X contact in organotellurium compounds

The study of Te···X contacts was based on analysis of data from Version 5.32 (last update of May 2011) of the Cambridge Structural Database (CSD) (Allen, 2002), where organic and organometallic crystal structures determined from X-ray (or neutron) diffraction data are deposited. A search was performed with the aid of the ConQuest program (Version 1.13) (Bruno et al., 2002) in order to retrieve crystal structures containing organotellurium compounds and halogen atoms. Only organic structures with available atomic coordinates were considered and several additional exclusion conditions were applied. Structures with R factor > 0.1, and structures where tellurium or halogen atoms are disordered, were omitted. Moreover, structures with charged fragments were also eliminated. After an additional checking to remove multiple entries of the same structure, a set of 481 structures was accepted. A search of intermolecular distances between tellurium and halogen atoms was performed and the results were analyzed using the Vista program (Version 2.1) (CCDC, 1994).

If a random distribution of halogens around tellurium atom is supposed, a distance histogram showing only an exponential growth would be expected. However this was not the case and a maximum was observed before the exponential growth (Figure 1). This maximum can be attributed to the existence of a Te···X interaction. A similar behaviour has been reported, for example, in O···O distance histograms where a H-bonding maximum has been observed (Rowland & Taylor, 1996). In the case of Te···F distances, most compounds are perfluorinated, introducing a bias in their distribution. When these compounds are removed, the remaining population size is so small that the resulting histogram is not statistically significant. When Te···X secondary and Te-X covalent bond distance ranges are compared, the former is broader (Table 1), according to the weaker nature of Te···X interaction. The maximum of the Te···X peak was located at a distance lower than the sum of van der Waals radii (Bondi, 1964) eventhough the peak spreads beyond this reference value. The sum of van der Waals radii is highly used in order to determine whether an interaction is present or not. However, this value is rather arbitrary (it is an approximation) and it can not be considered as a cut-off. In fact, in the case of H-bonding the use of such cut-off criterium has been discouraged (Jeffrey & Saenger, 1991). So, in the case of Te···X, it seems that the interaction can be present beyond the sum of van der Waals radii although its force decreases, according with the electrostatic character of the interaction. The upper limit for the peak analysis has been situated at $1.10 \cdot \Sigma r_{vdW}$, corresponding approximately to the local minimum in the histogram (for X = Cl, Br, and I).

Two more considerations about Te···X distance ranges should be taken into account. The first one is the temperature effect on the distance. Half the structures used in the present study have been determined at low temperature. It is known that weak interaction distances are more temperature dependent than covalent bond distances (Forni et al., 2004). Two CSD structures, DMTEII and QIXZAY, showing Te···I contacts and measured both at 130K and at

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Fig. 1. Histograms for the distribution of intermolecular Te···X distances

room temperature (see section 3.8), are well suited to carry out a distance comparison. In the case of QIXZAY the 130K experiment reveals a mean Te···I shortening of 0.050 Å while the mean Te-I bond shortening is just 0.005 Å, close to the experimental error (0.002 Å). DMTEII behaves in a similar way being the Te···I shortening even greater: 0.082 Å. So, every peak in the distance histograms is, in fact, the superposition of two peaks. However, the estimated difference in maximum positions (0.05 Å) is small compared with the peak width. Moreover, the number of structures defining every peak is not big enough to undertake a study of the temperature effect. The second consideration is the potential relation of Te···X distances vs the tellurium coordination. Eventhough this dependence should be expected, no differences were found. A greater number of structures may help to establish this dependence. In this context, a study carried out on tellurium supramolecular synthons established that no correlation exists between secondary bond distance and the coordination number of tellurium (Cozzolino et al., 2011).
The existence of intermolecular Te···X interactions is frequent in crystal structures of organotellurium compounds containing halogen atoms. Using the values showed in Table 1, the estimation of structures with Te···X interactions is about 60%. Of the total number of structures showing Te···X contacts, 13% of them exhibit Te···F interaction, 38%, Te···Cl, 20%, Te···Br and 29%, Te···I.

|       | d(σ)      | q₁₀, q₉₀      | n    |
|-------|-----------|---------------|------|
| Te···F| 3.26(11)  | 2.96, 3.80    | 10   |
| Te-F  | 1.989(4)  | 1.95, 2.02    | 43   |
| σ rvdW| 3.53      |               |      |
| Te···Cl| 3.672(15)| 3.42, 3.97    | 191  |
| Te-Cl | 2.521(3)  | 2.47, 2.61    | 546  |
| σ rvdW| 3.81      |               |      |
| Te···Br| 3.88(2)   | 3.56, 4.25    | 121  |
| Te-Br | 2.693(5)  | 2.63, 2.79    | 234  |
| σ rvdW| 3.91      |               |      |
| Te···I | 3.95(2)   | 3.67, 4.37    | 203  |
| Te-I  | 2.944(4)  | 2.87, 3.04    | 383  |
| σ rvdW| 4.04      |               |      |

Table 1. Te···X secondary and Te-X covalent bond distances (Å) in organotellurium crystal structures. The sum of van der Waals radii (Bondi, 1964), σ rvdw, is also included. d: mean value; σ: mean standard deviation; q₁₀, q₉₀: 10% and 90% percentiles; n: number of observations; covalent bond distances have been obtained in this work from organotellurium(IV) crystal structures from CSD

3. Supramolecular arrangements in organotellurium compounds

3.1 Method
A CSD search considering organic structures with deposited atomic coordinates, with R factor < 0.1, and without disorder involving Te and X was undertaken. After removing multiple entries of the same structure, a new search was carried out in order to retrieve structures showing intermolecular Te···X contacts. According to the results presented in section 2, a cut-off of σ rvdw + 10% Å was considered. In these structures, supramolecular patterns were investigated using the program Mercury (Version 2.4) (Macrae et al., 2008). A set of 616 organotellurium structures having halogen atoms was collected. The greater part of them, 490 (80%), contain the Te-X unit, i.e. at least one tellurium-halogen covalent bond. Four groups can be considered: (i) structures containing tellurium atoms with only one halogen atom bonded to it, i.e. having the C-Te(-X)₁ unit, (ii) structures containing tellurium atoms bonded to only two halogen atoms, i.e. having the C-Te(-X)₂ unit, (iii)
structures containing tellurium atoms with only three halogen atoms bonded to it, i.e. having the C-Te(-X)$_3$ unit, and (iv) structures containing tellurium atoms bonded to four halogen atoms, i.e. having the C-Te(-X)$_4$ unit. A fifth group (v) includes the remaining 126 structures of organotellurium compounds having halogen atoms but not Te-X units: structures with C-Te(-X)$_0$.

### 3.2 Structures of compounds containing the Te(-X)$_1$ unit

Te(-X)$_1$ unit (tellurium atom bonded to one halogen only), is a very simple unit and it is a good starting point to study supramolecular arrangements via Te···X contacts. Two arrangements are the more habitual in this group: (a) dimeric assembly, and (b) simple chain (Figure 2, Table 2).

![Fig. 2. Main supramolecular arrangements of compounds containing the Te(-X)$_1$ unit](image)

|        | F | Cl | Br | I | Total |
|--------|---|----|----|---|-------|
| Dimer  | 0 | 10 | 12 | 9 | 31    |
| Simple chain | 2 | 6  | 3  | 3 | 14    |
| Total  | 2 | 16 | 15 | 12| 45    |

Table 2. Summary of structures containing the Te(-X)$_1$ unit

a. In the dimer, the two Te-X rods are bonded by two Te···X secondary bonds. The majority is centrosymmetric, with X···Te-X angles around 90°.

In C-Te(II)-X (X = Cl, Br, I) compounds, dimers were observed. These compounds are not stable and the secondary bond stabilizes them. A new pattern is observed when weaker secondary bonds are considered (contact distances < Σ $r_{vdW} + 20\%$): a chain of dimers like a zigzag ladder (Figure 3) where two neighbour dimers are related by a symmetry centre. In this way, three TeX distances are present, being the Te-X rod length the shortest one. A great dispersion of distances was observed, not only in secondary bonds but in the “primary” bond as well.

Dimeric arrays were also observed in some molecules containing several Te-X units. In these cases the covalent skeleton increases the dimensionality of the whole arrangement. In this way, if two Te-X units are present, the structure contains chains, if there are four Te-X units by molecule, a sheet of dimers is formed (Figure 4).

b. In the simple chain, every rod is bonded to its neighbour using only one secondary bond. In some cases the chain is planar and neighbour rods are equivalent by translation. In the other cases, chains are generated by a screw binary axis or by a glide plane.
3.3 Structures of compounds containing the Te(-X)₂ unit

The most populated group of organotellurium compounds contains the C-Te(-X)₂ unit (only two halogen atoms bonded to tellurium). A lot of them have a C₂TeX₂ core showing a pseudotrigonal bipyramidal disposition with the halogen atoms in axial positions and a lone electron pair in an equatorial site (Figure 5).

A great diversity of arrangements is present in this group. Three of such arrangements are clearly the most usual: (a) dimer, (b) simple chain, and (c) chain of four-sided rings sharing opposite vertices. Other three arrangements, with more complicated patterns of secondary bonds, have also significant populations: (d) tetramer, (e) sheet, and (f) 3D-network (Figure 6, Table 3).
Fig. 6. Main supramolecular arrangements of compounds containing the Te(-X)$_2$ unit
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|                  | F | Cl | Br | I | Total |
|------------------|---|----|----|---|-------|
| Dimer            | 2 | 18 | 7  | 18| 45    |
| Simple chain     | 0 | 17 | 10 | 4 | 31    |
| Chain of 4-membered rings | 2 | 11 | 5  | 6 | 24    |
| Tetramer         | 0 | 5  | 1  | 3 | 9     |
| Sheet            | 0 | 2  | 0  | 2 | 4     |
| 3D-Network       | 0 | 1  | 2  | 2 | 5     |
| Less frequent arrangements | 2 | 1  | 2  | 3 | 8     |
| Total            | 6 | 55 | 27 | 38| 126   |

Table 3. Summary of structures containing the Te(-X)\(_2\) unit

a. Dimers formed by Te(-X)\(_2\) have the same connectivity as those described for Te(-X)\(_1\), i.e. two Te···X secondary bonds, and the majority are also centrosymmetric. Non centrosymmetric dimers are almost planar in absence of other interactions. Most X-Te···X angles are lesser than 90°, i.e. two rods are “moved away” relative to the rectangular disposition. This is a small difference respect to the Te(-X)\(_1\) dimers, where deviation from 90° were present in both directions. Only three dimers of angular Te(-X)\(_2\) were found, centrosymmetric all of them.

b. The Te(-X)\(_2\) simple chain is also referable to Te(-X)\(_1\) simple chains but here, planar chains are absent, the reason being that planar chains have the translation as unique symmetry element. In the case of Te(-X)\(_2\), this would imply the presence of an additional Te···X contact leading to a different kind of chain. So, rods in Te(-X)\(_2\) simple chains are equivalent by screw binary axes or by glide planes.

c. The third most common arrangement is a di-bridged chain made by 4-membered rings sharing opposite vertices (Te atoms). Three types of chain (polymer) can be considered when Te···X distances are analyzed. So, if 4-membered rings are not equal (6 structures), a dimer is present and this type of polymer will be named chain of dimers. If all 4-membered rings are equal, the basic unit in the polymer is an X-Te-X rod and two cases are possible. In the more symmetric one (7 structures), the two secondary bonds between neighbour rods are equal while in the less symmetric one (11 structures) are not. These two types of polymer will be named 1d- and 2d-polymer respectively. The three types of chain have also different internal symmetry. In the chains of dimers, 4-membered rings are centrosymmetric (rhomboids) and are disposed in zigzag. In six of the more symmetric polymers, there are symmetry centres in the middle of all rings, and moreover, binary axes, perpendicular to the chain direction, through the Te atoms, and glide planes. One symmetric polymer is helical, generated by a screw 4-fold axis, vs the zigzag disposition found in the other 6 structures. At last, polymers with two different secondary bonds between neighbours are generated by glide planes and adopt a zigzag conformation.

d. Another finite arrangement of Te(-X)\(_2\) is a cyclic tetramer, where a Te(-X)\(_2\) unit is bonded to every neighbour with two secondary bonds in a step-like manner. The tetramer has two different types of tellurium atoms: the two “middle” Te atoms defining a Te\(_2\)X\(_2\) ring are different from the two “terminal” Te atoms placed out of the Te\(_2\)X\(_2\) ring.
This arrangement implies the existence of two non-equivalent rods, thus forcing the structure to have more than one molecule in the asymmetric unit ($Z' > 1$). All the tetramers found are centrosymmetric.

e. Five structures with infrequent spatial groups ($Fd d 2$ and $I 4_1/acd$) adopt a symmetric polar 3D-network where all secondary bonds are equal. Every Te(-X)$_2$ rod is bonded to four neighbours, with two bonds from Te and one from every halogen.

f. A sheet with two secondary bond distances and where every rod is bonded to three neighbours is relatively usual. This arrangement can be described in two ways, depending on the distance ratio. In two structures, the best description is to consider them as centrosymmetric dimers (type (a)) bonded to four neighbours, involving the two Te and the two distant halogens of the dimer. For another two structures it is better to think in simple chains (type (b)) where every rod is bonded to another rod of a neighbouring chain by means of two Te···X bonds. Anyway, 4- and 12-membered rings are present.

g. Finally, four pairs of structures were found, each pair with its own arrangement: two chains and two sheets (Figure 7).

![Fig. 7. Less frequent supramolecular arrangements of compounds containing the Te(-X)$_2$ unit: $C_c$ and $C_d$ chains; $S_c$ and $S_d$ sheets](#)

### 3.4 Structures of compounds containing the Te(-X)$_3$ unit

This unit shows a T disposition derived of the tendency of halogen atoms to occupy axial positions (angle X-Te-X near to 180°). The dimeric arrangement (a) is adopted by most structures. The simple chain (b) and the chain of 4-membered rings (c) are present but are much less usual (Figure 8, Table 4).
Fig. 8. Main supramolecular arrangements of compounds containing the Te(-X)$_3$ unit: dimer (D); simple chain involving only axial halogen atoms (SC) or equatorial halogen atoms (SC-eq); 4-membered ring chain: chain of dimers (RC-CD), 2d-polymer involving only axial halogen atoms (RC-2d), and 2d-polymer involving equatorial (RC-2d-eq) halogen atoms.

|                | F  | Cl | Br | I  | Total |
|----------------|----|----|----|----|-------|
| **Dimer**      | 0  | 10 | 4  | 3  | 17    |
| **Simple chain**| 0  | 3  | 1  | 1  | 5     |
| **Chain of 4-membered rings** | 1  | 1  | 2  | 1  | 5     |
| **Total**      | 1  | 14 | 7  | 5  | 27    |

Table 4. Summary of structures containing the Te(-X)$_3$ unit

a. Dimer. As in Te(-X)$_1$ and Te(-X)$_2$ dimers, two units are linked by two secondary bonds. Axial halogen atoms are involved in them. Dimers are centrosymmetric and the equatorial halogen atom can be in different orientations. In most cases, the angle between the Te-X$_{eq}$ bond and the normal to planar core is less than 20º but in three cases this angle is significantly higher, 37-53º.
b. Simple chain. As in Te(-X)$_1$ and Te(-X)$_2$ simple chains, two units Te(-X)$_3$ are linked by one Te···X secondary bond. The link involves either axial (3 structures) or equatorial halogen (2 structures). As in Te(-X)$_2$ chains, units in Te(-X)$_3$ simple chains are equivalent by screw axes or by glide planes. It is remarkable that in one case, the screw axis is ternary and the chain turns to be helical, vs the zigzag disposition of the chains where binary screw axes are present.
c. In chains of 4-membered rings two cases have been found. In one of them, rings are defined by one axial halogen and the equatorial one. Chains are polymers with two Te···X distances (screw binary axis). In the other case, analogous to the Te(-X)$_2$ 4-membered ring chains, rings are defined only by axial halogen atoms and two
dispositions can be adopted: chain of dimers (centrosymmetric rings) and polymer with two Te···X distances (glide planes).

3.5 Structures of compounds containing the Te(-X)$_4$ unit
These compounds are ionic (or zwitterionic) and the coordination around the Te can be described as a tetragonal pyramid with the halogens and the tellurium in the basal plane and the carbon in the apical position of the pyramid. Two supramolecular patterns are relevant: (a) dimers and (b) simple chains (Figure 9, Table 5).

![Fig. 9. Main supramolecular arrangements of compounds containing the Te(-X)$_4$ unit](image)

|       | F | Cl | Br | I | Total |
|-------|---|----|----|---|-------|
| Dimer | 0 | 6  | 4  | 6 | 16    |
| Simple chain | 0 | 2  | 3  | 2 | 7     |
| Total   | 0 | 8  | 7  | 8 | 23    |

Table 5. Summary of structures containing the Te(-X)$_4$ unit

a. Dimers. As in Te(-X)$_1$, Te(-X)$_2$ and Te(-X)$_3$, dimers contain two secondary bonds. These bonds complete an octahedral coordination for every Te. All dimers are centrosymmetric except one with a binary axis instead.
b. Simple chains. Again, the secondary bond completes the octahedral coordination of tellurium atom. As in Te(-X)$_2$ and Te(-X)$_3$ chains, units in Te(-X)$_4$ simple chains are equivalent by screw axes or by glide planes.

3.6 Structures of compounds without Te-X units [Te(-X)$_0$]
This group is very heterogeneous from a chemical point of view, nevertheless some subsets can be established (Figure 10). A first subset (12 structures) was considered where neutral molecules contain one Te and halogen atoms. This subset can be considered a general case of the compounds studied in the previous sections: now the tellurium atom and the halogens are separated by more than one covalent bond, hereinafter Te(---X)$_n$. Therefore some above described arrangements were also found here: dimer (4 structures), simple chain (2 structures), and chain of dimers (2 structures).
In a second subset of 11 neutral ditellurides, known patterns were also found in more than half the cases, considering them as X---Te(---X). Every Te---X unit affords its own arrangement of secondary bonds: dimers (3 structures), and simple chains (3 structures).
When Te-Te bridges are considered, arrangements of higher dimensionality can exist. For example, a Te-Te unit can be bridging dimers to afford a chain of dimers. Analogously, the combination of chains of secondary bonds and Te-Te bridges can give three more complex arrangements: (i) double chains, (ii) sheets composed by parallel chains, and (iii) double sheets linked by perpendicular Te-Te bridges in a grid-like array.

In other neutral molecules having two tellurium atoms separated by other atoms, single chains of secondary bonds linked by the Te···Te core were observed.

The rest of structures (50) are ionic. In 19 of them, tellurium atoms are in the cationic moiety, halogen atoms are in the anion, and one secondary bond links both ions to give an 1:1 adduct. More complex adducts exist when more than two ions or solvent molecules are bonded by Te···X bonds.

![Fig. 10. Examples of supramolecular arrangements in the Te(-X)\(_0\) group: dimer (D); simple chain (SC); chain of dimers (CD); specific sheet (S\(_e\)); adduct (A). Superscripts stand for the number of atoms between Te and X atoms](https://www.intechopen.com)

### 3.7 Additional structural considerations

#### 3.7.1 Polymorphism

A search for polymorphism was performed in order to study its relation with the arrangement. Eleven organotellurium compounds containing halogen atoms showed two polymorphic structures each one: two in the Te(-X)\(_1\) group, seven in the Te(-X)\(_2\) group, one in the Te(-X)\(_3\) group, and one in the Te(-X)\(_0\) group (Figure 11, Table 6). In ten cases, different
arrangements were observed for the polymorphic pair while in one case polymorphism is associated to a different packing of the same supramolecular entity (tetramers). Moreover, it is usual to observe a change of dimensionality between polymorphs.

![Diagram showing specific arrangements in polymorphic structures: Ta tetramer; Ca and Cb chains; Sa and Sb sheets](image-url)

**Fig. 11.** Some specific arrangements present in polymorphic structures: $T_a$ tetramer; $C_a$ and $C_b$ chains; $S_a$ and $S_b$ sheets
Table 6. Supramolecular arrangements found in polymorphic structures. 0 = no Te···X contacts; D = dimer; SC = simple chain; RC = chain of 4-membered rings; T = tetramer; N = 3D-network; C\textsubscript{a}, C\textsubscript{b}, T\textsubscript{a}, S\textsubscript{a}, S\textsubscript{b}: specific chains (Fig. 7); S\textsubscript{4}: specific chain (Fig. 10); C\textsubscript{a}, C\textsubscript{b}, T\textsubscript{a}, S\textsubscript{a}, S\textsubscript{b}: specific chains, tetramer, sheets (Fig. 11); N\textsubscript{a} specific 3D-network.

| Refcode         | S. G. | Arrang. | D\textsubscript{c} (g cm\textsuperscript{-3}) |
|-----------------|-------|---------|-----------------------------------------------|
| PAZPTE          | P-1 I2/a | T\textsubscript{a} | 1.942 1.966 |
| PAZPTE01        |       | C\textsubscript{a} |       |
| BTUPTE          | C2/c P2\textsubscript{1}/c | 0 D | 2.106 2.017 |
| BTUPTE01        |       |       |       |
| DIDMTE          | P2\textsubscript{1}/c C2/c | S\textsubscript{a} RC | 3.393 3.410 |
| DIDMTE01        |       |       |       |
| CIFLEI          | I4\textsubscript{1} P2\textsubscript{1}/c | N C\textsubscript{b} | 2.556 2.534 |
| CIFLEI01        |       |       |       |
| NUNHUZ          | P-1 P-1 | T T | 2.256 2.287 |
| NUNHUZ01        |       |       |       |
| SABCII          | Pn lbca | 0 D | 1.669 1.666 |
| SABCII01        |       |       |       |
| ASEHUB          | P2\textsubscript{1}/c P2\textsubscript{1}/a | 0 SC | 1.759 1.737 |
| ASEHUB01        |       |       |       |
| QIXZAY          | P2\textsubscript{1}/n P2\textsubscript{1}/c | C\textsubscript{c} C\textsubscript{d} | 3.138 3.263 |
| QIXZAY03        |       |       |       |
| DIBTEP02        | Fdd2 P2\textsubscript{1}/c | N S\textsubscript{b} | 2.843 2.887 |
| DIBTEP10        |       |       |       |
| BIPTTEI         | P2\textsubscript{1}/n P2\textsubscript{1}/c | SC D | 2.861 2.777 |
| BIPTTEI01       |       |       |       |
| CLPHTE          | P2\textsubscript{1}/n P2\textsubscript{1}2\textsubscript{1}2\textsubscript{1} | N\textsubscript{a} S\textsubscript{4} | 2.316 2.365 |
| CLPHTE01        |       |       |       |
3.7.2 Halogen series

The set of organotellurium structures containing halogen atoms includes three complete series of halo compounds with the same molecular structure but different halogen, X = F, Cl, Br, I (Table 7). In the three series, bromo and iodo members are isostructural. In the second series, the chloro compound is also isostructural. When isostructurality is not present, arrangements are different.

| Series | F   | Cl   | Br   | I    |
|--------|-----|------|------|------|
|        | KEHBIJ | BIBBOE | BIBCEV | QIXZAY |
|        | S_c  | S    | C_c  | C_c  |
|        |       |       |       |       |
|        | GETHOC | BIBCAR | BIBBUK | DIBTEP02 |
|        | S_c  | N    | N    | N    |
|        |       |       |       |       |
|        | FPHTEL | OPNTED10 | DPHTEB01 | CIFLEI |
|        | RC   | SC   | N    | N    |

Table 7. Supramolecular arrangements in complete halogen series. SC = simple chain; RC = chain of 4-membered rings; S = sheet; N = 3D-network; C_c, C_d, S_c: specific chains and sheet (Fig. 7); C_b, S_b: specific chain and sheet (Fig. 11)

Partial series of three and two members are also present in the set of compounds studied, and its abundance is significant: 20 and 47 series respectively. In these partial series, isostructurality is also frequent but examples of non-isostructural members with the same kind of supramolecular arrangement are present (Table 8).

| Series | F   | Cl   | Br   | I    |
|--------|-----|------|------|------|
|        |     | YASVAP | YASVET |
|        |     | RC    | RC    |
|        |     | IDEXY | IDEXOZ |
|        |     | RC    | RC    |
|        |     | TUWPAC | TUWPIK |
|        |     | RC    | RC    |

Table 8. Supramolecular arrangements in partial halogen series. RC = chain of 4-membered rings
3.8 Selection of structures
The following list collects relevant structures of this section (Table 9).

| Refcode   | Journal                  | Vol. | Page | Year |
|-----------|--------------------------|------|------|------|
| **Structures of compounds containing the Te(-X)\_2 unit** |
| **a) Dimers** |
| BSEUTE    | Acta Chem.Scand.A        | 29   | 763  | 1975 |
| BTUTPE01  | Acta Chem.Scand.A        | 29   | 738  | 1975 |
| BZETBS    | Acta Chem.Scand.         | 20   | 132  | 1966 |
| BZETCS    | Acta Chem.Scand.         | 20   | 132  | 1966 |
| CEHFAW    | Organometallics         | 18   | 803  | 1999 |
| CETUTE    | Acta Chem.Scand.A        | 29   | 763  | 1975 |
| DONQEC    | Inorg.Chem.              | 38   | 3994 | 1999 |
| DONQIG    | Inorg.Chem.              | 38   | 3994 | 1999 |
| DONQOM    | Inorg.Chem.              | 38   | 3994 | 1999 |
| ERIBIQ    | Organometallics         | 22   | 5473 | 2003 |
| GEDSEO    | Z.Kristallogr.           | 221  | 166  | 2006 |
| HIFVOH    | Acta Crystallogr., Sect.C| 52   | 424  | 1996 |
| OCICIN    | Chem.-Eur.J.             | 12   | 2515 | 2006 |
| OLODUO    | Acta Crystallogr., Sect.C| 59   | 571  | 2003 |
| OLOFAW    | Acta Crystallogr., Sect.C| 59   | 571  | 2003 |
| PETBIA    | Z.Anorg.Allg.Chem.       | 633  | 127  | 2007 |
| PETBIO    | Z.Anorg.Allg.Chem.       | 633  | 127  | 2007 |
| POYGEP    | J.Organomet.Chem.        | 549  | 257  | 1997 |
| POYGIT    | J.Organomet.Chem.        | 549  | 257  | 1997 |
| QANWEH    | J.Organomet.Chem.        | 605  | 39   | 2000 |
| QIYBAB    | J.Organomet.Chem.        | 623  | 74   | 2001 |
| QOKZIZ    | Polyhedron               | 20   | 203  | 2001 |
| ROCTAE    | Inorg.Chem.              | 36   | 1890 | 1997 |
| TEGZIP    | Acta Crystallogr., Sect.C| 52   | 2022 | 1996 |
| WEXBIK    | Khim.Get.Soedin., SSSR   | 417  |      | 1994 |
| WOMDIL    | Phosphorus, Sulfur, Silicon | 123  | 313  | 1997 |
| YEXWHI    | Inorg.Chem.              | 33   | 6154 | 1994 |
| YEXWON    | Inorg.Chem.              | 33   | 6154 | 1994 |
| YEXWUT    | Inorg.Chem.              | 33   | 6154 | 1994 |
| **Dimers connected by covalent skeleton** |
| HOJJEV01  | Angew.Chem., Int.Ed.     | 39   | 1796 | 2000 |
| REDXEE    | Eur.J.Inorg.Chem.        | 124  | 961  | 2006 |
| **b) Simple chains** |
| BRTEBA    | Acta Crystallogr., Sect.B| 35   | 849  | 1979 |
| CEHKEF    | Organometallics          | 18   | 803  | 1999 |
| CIDKIQ    | Inorg.Chem.              | 46   | 3275 | 2007 |
| JABWUE    | J.Am.Chem.Soc.           | 110  | 6762 | 1988 |
### Structures of compounds containing the Te(-X)₂ unit

#### a) Dimers

| Code  | Title                                      | Volume | Pages | Year |
|-------|--------------------------------------------|--------|-------|------|
| CIDKEG | *Inorg. Chem.*                             | 46     | 3275  | 2007 |
| CLPTEI | *Acta Crystallogr.*                        | 15     | 887   | 1962 |
| DMTEII | *Inorg. Chem.*                             | 18     | 311   | 1979 |
| GACXUD01 | *Acta Crystallogr., Sect. C*               | 47     | 703   | 1991 |
| GIPRED | *Angew. Chem., Int. Ed.*                   | 46     | 8277  | 2007 |
| GODKUG | *Z. Kristallogr.*                          | 223    | 536   | 2008 |
| HEXBOB | *Can. J. Chem.*                            | 72     | 1844  | 1994 |
| HOFKES | *Acta Crystallogr., Sect. C*               | 55     | 1339  | 1999 |
| JATSIG | *J. Chem. Soc., Dalton Trans.*             |        |       |      |
| KONYAB | *Acta Crystallogr., Sect. C*               | 47     | 1858  | 1991 |
| LAFNUB | *Z. Naturforsch., B: Chem. Sci.*           | 48     | 199   | 1993 |
| OCICUZ | *Chem.-Eur. J.*                            | 12     | 2515  | 2006 |
| OFUTOZ | *Dalton Trans.*                           |        | 4023  | 2008 |
| PEKLMU | *J. Crystallogr. Spectrosc. Res.*          | 23     | 181   | 1993 |
| SABCI01 | *Acta Crystallogr., Sect. E*               | 61     | o986  | 2005 |
| SEPMAB | *J. Chem. Soc., Dalton Trans.*             |        | 907   | 1990 |
| TUWNOO | *Dalton Trans.*                           |        | 973   | 2003 |
| TUWNUU | *Dalton Trans.*                           |        | 973   | 2003 |
| TUWPEG | *Dalton Trans.*                           |        | 973   | 2003 |
| UJAMIC | *J. Organomet. Chem.*                      | 695    | 2532  | 2010 |
| UJAMUC | *J. Organomet. Chem.*                      | 695    | 2532  | 2010 |
| UJORUH | *J. Organomet. Chem.*                      | 695    | 2118  | 2010 |
| UKAFAO | *Inorg. Chem.*                            | 49     | 7577  | 2010 |
| UKAFES | *Inorg. Chem.*                            | 49     | 7577  | 2010 |
| UKAIFIW | *Inorg. Chem.*                          | 49     | 7577  | 2010 |
| UKAFOC | *Inorg. Chem.*                            | 49     | 7577  | 2010 |
| UKAGET | *Inorg. Chem.*                            | 49     | 7577  | 2010 |
| UKAGIX | *Inorg. Chem.*                            | 49     | 7577  | 2010 |
| VOHVET | *J. Organomet. Chem.*                      | 418    | 339   | 1991 |
| WECQIF | *Z. Anorg. Allg. Chem.*                    | 632    | 659   | 2006 |
| WECQOL | *Z. Anorg. Allg. Chem.*                    | 632    | 659   | 2006 |
| WIDZOO | *Z. Anorg. Allg. Chem.*                    | 633    | 1261  | 2007 |
### b) Simple chains

| Code   | Journal                                    | Volume | Pages  | Year |
|--------|--------------------------------------------|--------|--------|------|
| ASEHUB01 | Z.Kristallogr.                             | 218    | 636    | 2003 |
| BOQJIA | Acta Crystallogr., Sect. C                 | 55     | 1930   | 1999 |
| CEDDAQ | J.Org.Chem.                                | 48     | 5149   | 1983 |
| CEJP AJ| Heteroat.Chem.                             | 16     | 316    | 2005 |
| CLCHTE | Cryst.Struct.Commun.                       | 9      | 533    | 1980 |
| GOKFAO | Z.Kristallogr.                             | 223    | 536    | 2008 |
| IDEXEU | Inorg.Chem.                                | 40     | 5169   | 2001 |
| JILXAD | Acta Crystallogr., Sect. C                | 47     | 960    | 1991 |
| KAKCOP | Aust.J.Chem.                               | 58     | 119    | 2005 |
| KEQCIT | Inorg.Chim.Acta                            | 359    | 4619   | 2006 |
| MIDWAY | Struct.Chem.                               | 18     | 181    | 2007 |
| NIJJQM | Polyhedron                                 | 16     | 2441   | 1997 |
| OFUVER | Dalton Trans.                             | 4023   | 2008   |
| OFUVIV | Dalton Trans.                             | 4023   | 2008   |
| OPNITED10 | J.Chem.Soc., Dalton Trans.                | 251    | 1982   |
| QOGPAD | Acta Crystallogr., Sect. C                | 57     | 749    | 2001 |
| SEJPIG | Acta Crystallogr., Sect. C                | 46     | 251    | 1990 |
| STECHB | Inorg.Chem.                                | 11     | 3026   | 1972 |
| TLCLTE | Cryst.Struct.Commun.                       | 9      | 539    | 1980 |
| UIJOSAO | J.Organomet.Chem.                          | 695    | 2118   | 2010 |
| UIJOSOC | J.Organomet.Chem.                          | 695    | 2118   | 2010 |
| VUZJJ | Acta Crystallogr., Sect. C                | 44     | 2182   | 1988 |
| XUCNIS | Chin.J.Chem.                               | 19     | 457    | 2001 |
| XUCNOY | Chin.J.Chem.                               | 19     | 457    | 2001 |
| XRRAE | Dalton Trans.                             | 39     | 2637   | 2010 |
| XURSEJ | Dalton Trans.                             | 39     | 2637   | 2010 |
| YOWMEC | Acta Crystallogr., Sect. C                | 51     | 861    | 1995 |
| YUFNUI | Z.Kristallogr.                             | 210    | 306    | 1995 |

### c) Chains of 4-membered rings

| Code   | Journal                                    | Volume | Pages  | Year |
|--------|--------------------------------------------|--------|--------|------|
| BZTELI10 | Inorg.Chem.                               | 14     | 1142   | 1975 |
| CEGNOR | J.Chem.Soc., Dalton Trans.                | 23     | 1984   |
| HIQSUV | Acta Crystallogr., Sect. C                | 55     | 648    | 1999 |
| IDEXIY | Inorg.Chem.                                | 40     | 5169   | 2001 |
| PTELDI10 | Inorg.Chem.                               | 12     | 2669   | 1973 |
| YASVAP | Z.Anorg.Allg.Chem.                         | 619    | 1269   | 1993 |
| YASVET | Z.Anorg.Allg.Chem.                         | 619    | 1269   | 1993 |
### d) Tetramers

| Reference   | Journal/Conference          | Volume | Issue | Year |
|-------------|----------------------------|--------|-------|------|
| IDEXOE      | Inorg.Chem.                 | 40     | 5169  | 2001 |
| IDEXUK      | Inorg.Chem.                 | 40     | 5169  | 2001 |
| LEVKED      | J.Am.Chem.Soc.              | 128    | 14949 | 2006 |
| MIHFIS      | J.Flourine Chem.            | 102    | 301   | 2000 |
| TUWNII      | Dalton Trans.               |        | 973   | 2003 |
| TUWPAC      | Dalton Trans.               |        | 973   | 2003 |
| TUWPIK      | Dalton Trans.               |        | 973   | 2003 |
| UKAFUI      | Inorg.Chem.                 | 49     | 7577  | 2010 |
| UKAGAP      | Inorg.Chem.                 | 49     | 7577  | 2010 |
| VOTSIG      | Organometallics             | 11     | 954   | 1992 |
| XUPXAI      | Heterocycles                | 80     | 1339  | 2010 |
| CERWIF      | J.Organomet.Chem.           | 262    | 151   | 1984 |
| COBPOY      | J.Organomet.Chem.           | 268    | 141   | 1984 |
| DIDMTE01    | Dalton Trans.               |        | 6274  | 2008 |
| FPHTEL      | J.Chem.Soc., Dalton Trans.  |        | 2306  | 1980 |
| MIHFEO      | J.Flourine Chem.            | 102    | 301   | 2000 |
| YUPHIB      | Z.Anorg.Allg.Chem.          | 635    | 862   | 2009 |

### e) Sheets

| Reference   | Journal/Conference          | Volume | Issue | Year |
|-------------|----------------------------|--------|-------|------|
| BOHNAN      | Acta Crystallogr., Sect.C   | 39     | 45    | 1983 |
| BUNDIY      | Inorg.Chem.                 | 48     | 10330 | 2009 |
| CIMFOT      | Acta Crystallogr., Sect.C   | 40     | 1349  | 1984 |
| IHOFIU      | J.Organomet.Chem.           | 669    | 149   | 2003 |
| LIMZEM      | Acta Crystallogr., Sect.C   | 51     | 639   | 1995 |
| NUNHUZ      | Acta Crystallogr., Sect.C   | 54     | 995   | 1998 |
| NUNHUZ01    | Acta Crystallogr., Sect.C   | 54     | 995   | 1998 |
| PHTECL      | Inorg.Chem.                 | 19     | 2556  | 1980 |
| PIXPES      | J.Organomet.Chem.           | 693    | 957   | 2008 |

### f) 3D-Networks

| Reference   | Journal/Conference          | Volume | Issue | Year |
|-------------|----------------------------|--------|-------|------|
| BIBBUK      | Polyhedron                  | 23     | 1629  | 2004 |
| BBCAR       | Polyhedron                  | 23     | 1629  | 2004 |
| CIFLEI      | J.Chem.Soc., Dalton Trans.  | 869    |       | 1984 |
| DIBTEP02    | Inorg.Chem.                 | 24     | 1814  | 1985 |
| DPHTEB01    | Acta Crystallogr., Sect.E   | 60     | o2511 | 2004 |

### g) Less frequent arrangements

| Reference   | Journal/Conference          | Volume | Issue | Year |
|-------------|----------------------------|--------|-------|------|
| BIBCEV      | Polyhedron                  | 23     | 1629  | 2004 |
| QIXZAY      | J.Organomet.Chem.           | 623    | 74    | 2001 |
| QIXZAY03    | Inorg.Chem.                 | 43     | 3742  | 2004 |
| SIDGIW      | Struct.Chem.                | 18     | 223   | 2007 |
| COQNOL01    | Inorg.Chem.                 | 38     | 3994  | 1999 |
Structures of compounds containing the Te(-X)₃ unit

**a) Dimers**

| Code  | Journal                        | Year | Volume | Page |
|-------|--------------------------------|------|--------|------|
| AZOFAW | J.Organomet.Chem.              | 2004 | 689    | 2092 |
| BIPTEI01 | Inorg.Chem.                   | 1977 | 16     | 2318 |
| BPYTEB | Inorg.Chem.                   | 1977 | 16     | 612  |
| CIDKAC | Inorg.Chem.                   | 2007 | 46     | 3275 |
| CUBFIP | Inorg.Chem.                   | 2009 | 48     | 3239 |
| DEFHAX | Acta Crystallogr., Sect.C     | 1985 | 41     | 1545 |
| EOCTEC | J.Organomet.Chem.             | 1979 | 181    | 335  |
| GEHDIH | Z.Anorg.Alg.Chem.             | 2006 | 632    | 893  |
| GEHDON | Z.Anorg.Alg.Chem.             | 2006 | 632    | 893  |
| GIZJEE | J.Chem.Soc., Dalton Trans.    | 1988 | 2363   |      |
| GOPLEC | Polyhedron                    | 1998 | 17     | 2153 |
| IMOZUF | Organometallics               | 2003 | 22     | 5069 |
| SEPLUU | J.Chem.Soc., Dalton Trans.    | 1990 | 907    |      |
| WEQVAP | J.Organomet.Chem.             | 2000 | 598    | 49   |
| XOPROK | Angew.Chem., Int.Ed.          | 2008 | 47     | 9982 |
| ZATROB | Z.Kristallogr.                | 1995 | 210    | 552  |

**b) Simple chains**

| Code  | Journal                        | Year | Volume | Page |
|-------|--------------------------------|------|--------|------|
| BONHUH | Cryst.Struct.Commun.           | 1982 | 11     | 1593 |
| DOTLUT | J.Org.Chem.                    | 1986 | 51     | 1692 |
| PAFLIR | Inorg.Chem.                    | 1992 | 31     | 1431 |
| BIPTEI | Inorg.Chem.                    | 1976 | 15     | 2728 |
| UDHUW  | Organometallics                | 2002 | 21     | 526  |

**c) Chains of 4-membered rings**

| Code  | Journal                        | Year | Volume | Page |
|-------|--------------------------------|------|--------|------|
| WEQVET | J.Organomet.Chem.              | 2000 | 598    | 49   |
| MUWBIP | J.Organomet.Chem.              | 2002 | 664    | 306  |
| OLODIOI | Acta Crystallogr., Sect.C     | 2003 | 59     | 0571 |
| WERWUM | J.Organomet.Chem.              | 2006 | 691    | 4807 |
| YIHRAJ | Z.Anorg.Alg.Chem.              | 2007 | 633    | 1618 |

Structures of compounds containing the Te(-X)₄ unit

**a) Dimers**

| Code  | Journal                        | Year | Volume | Page |
|-------|--------------------------------|------|--------|------|
| CIFVOD | J.Organomet.Chem.              | 2007 | 692    | 3081 |
| CIFVUJ | J.Organomet.Chem.              | 2007 | 692    | 3081 |
| CIFWAQ | J.Organomet.Chem.              | 2007 | 692    | 3081 |
| CITMAT | Tetrahedron                    | 1984 | 40     | 1607 |
| CUCGOW | Can.J.Chem.                    | 1984 | 62     | 32   |
| DEBXOY | Appl.Organomet.Chem.           | 2005 | 19     | 1196 |
| DEBXUE | Appl.Organomet.Chem.           | 2005 | 19     | 1196 |
Supramolecular Arrangements in Organotellurium Compounds via Te··· Halogen Contacts

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ELAVAP Inorg.Chim.Acta 365 492 2011
IHIMAO J.Organomet.Chem. 694 2463 2009
IHIMES J.Organomet.Chem. 694 2463 2009
JASCAL Z.Anorg.Allg.Chem. 631 1524 2005
MECGEH Eur.J.Inorg.Chem. 958 2006
MECGOR Eur.J.Inorg.Chem. 958 2006
MTEMTE J.Chem.Soc.A 2018 1967
WUGVUQ J.Braz.Chem.Soc. 17 1566 2006
WUTJOK Z.Anorg.Allg.Chem. 629 215 2003

b) Simple chains
IJOHUK Inorg.Chem.Commun. 6 869 2003
IJOJAS Inorg.Chem.Commun. 6 869 2003
JASBUB Z.Anorg.Allg.Chem. 631 1524 2005
KEQCAL Inorg.Chim.Acta 359 4619 2006
MECGUX Eur.J.Inorg.Chem. 958 2006
WUGVIE J.Braz.Chem.Soc. 17 1566 2006
WUGVOK J.Braz.Chem.Soc. 17 1566 2006

Structures of compounds without Te-X units [Te(-X)$_n$] in Figure
CLPHTE01 Acta Crystallogr.,Sect.C 40 1011 1984
DIHHAE Bioinorg.Chem.Appl. 69263 2007
JATWAC Inorg.Chem. 38 519 1999
JEPBAH Acta Chem.Scand. 44 464 1990
YABXEF J.Fluorine Chem. 125 997 2004

Polymorphs
ASEHUB Z.Kristallogr. 218 636 2003
ASEHUB01 Z.Kristallogr. 218 636 2003
BIPTIE Inorg.Chem. 15 2728 1976
BIPTIE01 Inorg.Chem. 16 2318 1977
BTUPTE Acta Chem.Scand.A 29 738 1975
BTUPTE01 Acta Chem.Scand.A 29 738 1975
CIFLEI J.Chem.Soc.,Dalton Trans. 869 1984
CIFLEI01 J.Chem.Soc.,Dalton Trans. 869 1984
CLPHTE Acta Crystallogr 10 201 1957
CLPHTE01 Acta Crystallogr.,Sect.C 40 1011 1984
DIBTEP10 J.Organomet.Chem. 178 423 1979
DIDMTE J.Chem.Soc.,Dalton Trans. 316 1972
DIDMTE01 Dalton Trans. 6274 2008
NUNHUZ Acta Crystallogr.,Sect.C 54 995 1998
NUNHUZ01 Acta Crystallogr.,Sect.C 54 995 1998
PAZPTE J.Chem.Res. 145 1901 1979
PAZPTE01 J.Organomet.Chem. 549 257 1997
QIXZAY J.Organomet.Chem. 623 74 2001
Table 9. Short-form references to individual CSD entries. In blue, structures measured at low temperature

**4. Conclusion**

In the majority of structures having tellurium and halogens, intermolecular Te···X contacts are observed.

Despite the great chemical diversity found in these compounds, the majority of them can be grouped considering only a few supramolecular patterns, *i.e.*, dimer, simple chain and chain of 4-membered rings.

Isostructurality is frequent in series of compounds with the same molecular structure but different halogen and, moreover, in some non isostructural compounds the supramolecular arrangement is retained.

No relations have been found between supramolecular arrangements of polymorphs although due to the reduced number of cases can not ruled them out.
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This book on X-ray Crystallography is a compilation of current trends in the use of X-ray crystallography and related structural determination methods in various fields. The methods covered here include single crystal small-molecule X-ray crystallography, macromolecular (protein) single crystal X-ray crystallography, and scattering and spectroscopic complimentary methods. The fields range from simple organic compounds, metal complexes to proteins, and also cover the meta-analyses of the database for weak interactions.

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