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Supramolecular Arrangements in Organotellurium Compounds *via* Te...Halogen Contacts

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In memory of Professor Gabriel Germain, for his guidance and his friendship

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.), $\pi \cdots \pi$ interactions, halogen bonds, cation $\cdots \pi$ 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; Petraghani & 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 \cdots 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 \cdots halogen (Te \cdots 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) even though 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 $1.10 \cdot \sum r_{vdW}$, 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

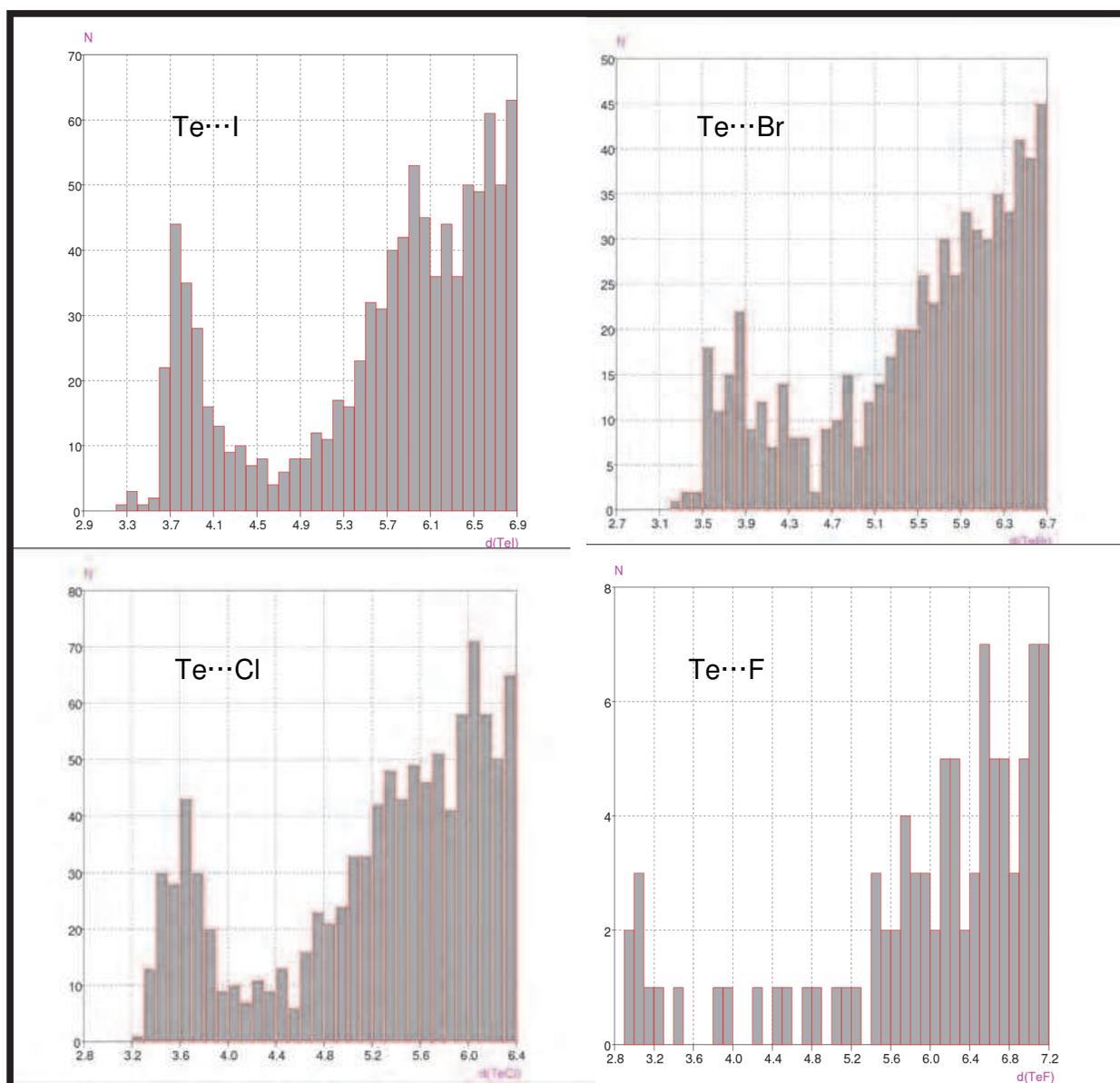


Fig. 1. Histograms for the distribution of intermolecular Te···X distances

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 $\text{Te}\cdots\text{X}$ interactions is frequent in crystal structures of organotellurium compounds containing halogen atoms. Using the values showed in Table 1, the estimation of structures with $\text{Te}\cdots\text{X}$ interactions is about 60%. Of the total number of structures showing $\text{Te}\cdots\text{X}$ contacts, 13% of them exhibit $\text{Te}\cdots\text{F}$ interaction, 38%, $\text{Te}\cdots\text{Cl}$, 20%, $\text{Te}\cdots\text{Br}$ and 29%, $\text{Te}\cdots\text{I}$.

	$d(\sigma)$	q_{10}, q_{90}	n
Te\cdotsF	3.26(11)	2.96, 3.80	10
Te-F	1.989(4)	1.95, 2.02	43
Σr_{vdW}	3.53		
Te\cdotsCl	3.672(15)	3.42, 3.97	191
Te-Cl	2.521 (3)	2.47, 2.61	546
Σr_{vdW}	3.81		
Te\cdotsBr	3.88 (2)	3.56, 4.25	121
Te-Br	2.693(5)	2.63, 2.79	234
Σr_{vdW}	3.91		
Te\cdotsI	3.95 (2)	3.67, 4.37	203
Te-I	2.944(4)	2.87, 3.04	383
Σr_{vdW}	4.04		

Table 1. $\text{Te}\cdots\text{X}$ secondary and Te-X covalent bond distances (\AA) in organotellurium crystal structures. The sum of van der Waals radii (Bondi, 1964), Σr_{vdW} , is also included. d : mean value; σ : mean standard deviation; q_{10}, q_{90} : 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 $\text{Te}\cdots\text{X}$ contacts. According to the results presented in section 2, a cut-off of $\Sigma r_{vdW} + 10\% \text{\AA}$ 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).

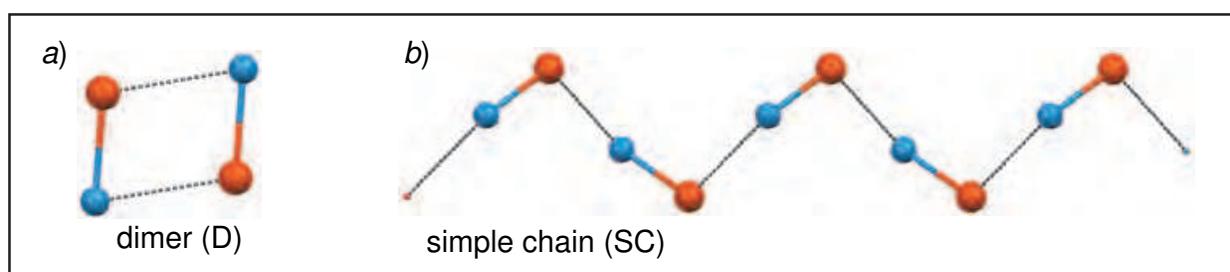


Fig. 2. Main supramolecular arrangements of compounds containing the Te(-X)₁ unit

	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

- 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 < $\Sigma r_{vdw} + 20\%$): 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).
- 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.

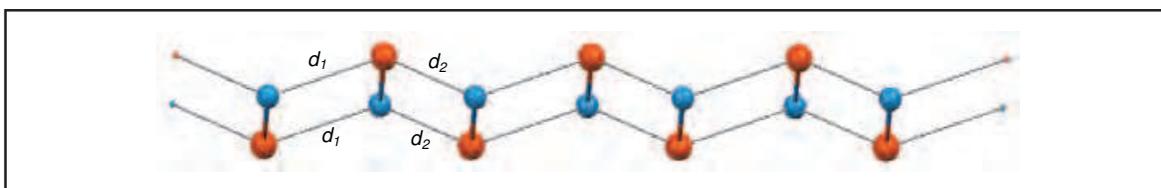


Fig. 3. Chain of dimers like a zigzag ladder ($d_1 > d_2$)

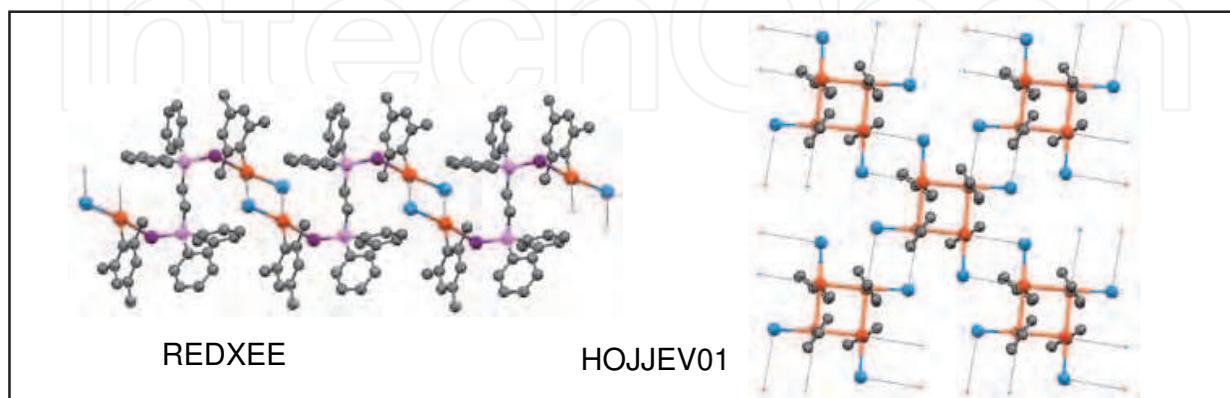


Fig. 4. Examples of chain and sheet resulting from the combination of dimers and a covalent skeleton

3.3 Structures of compounds containing the $\text{Te}(-\text{X})_2$ unit

The most populated group of organotellurium compounds contains the $\text{C}-\text{Te}(-\text{X})_2$ unit (only two halogen atoms bonded to tellurium). A lot of them have a C_2TeX_2 core showing a pseudotrigonal bipyramidal disposition with the halogen atoms in axial positions and a lone electron pair in an equatorial site (Figure 5).

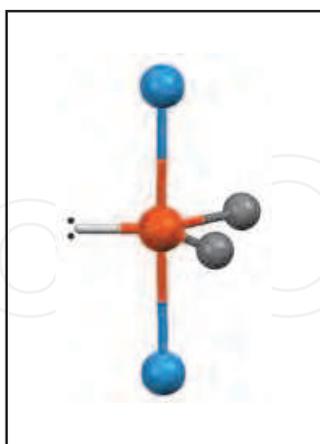
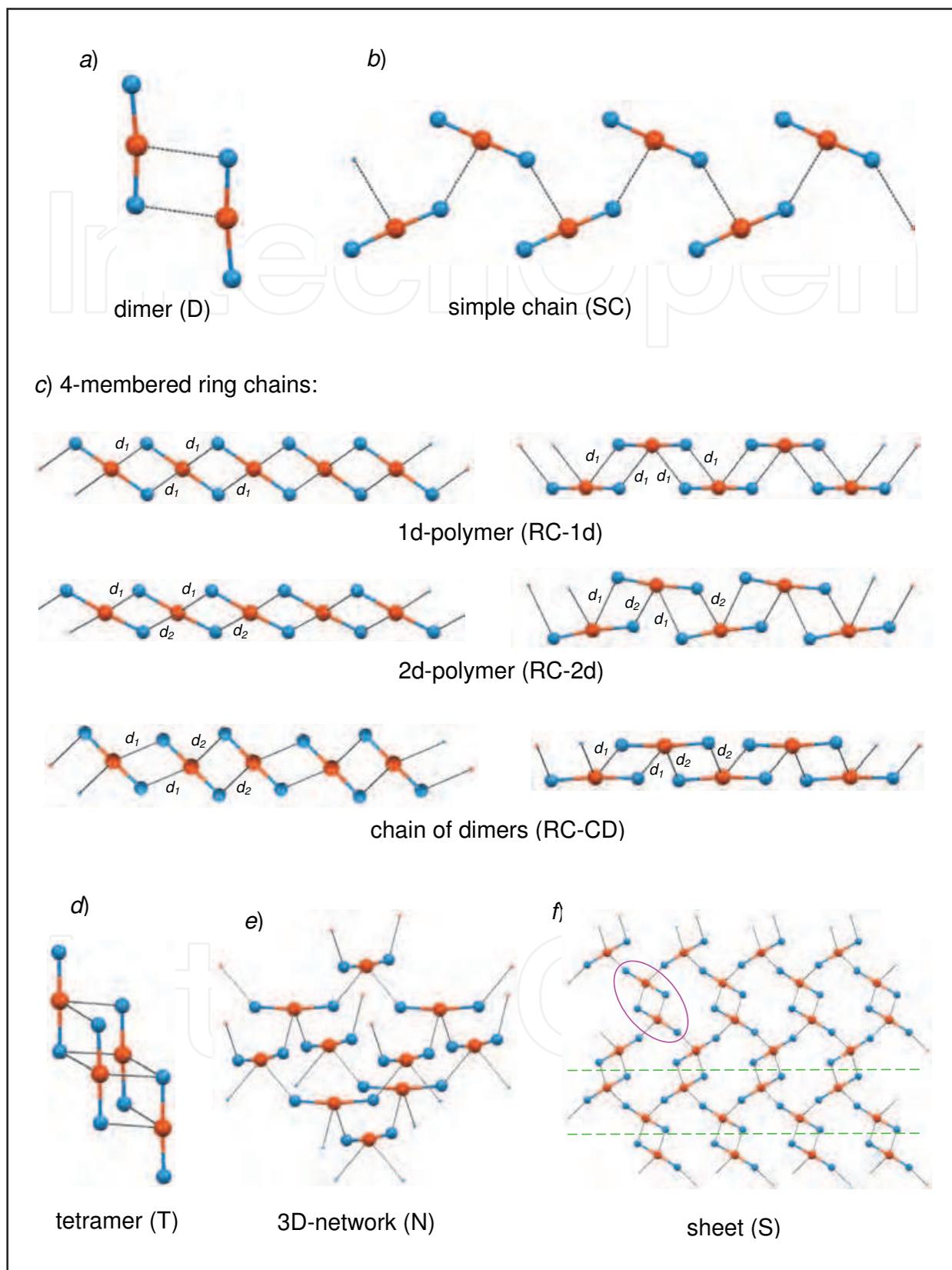


Fig. 5. Pseudotrigonal bipyramidal coordination frequent in R_2TeX_2 compounds

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 $\text{Te}(-\text{X})_2$ unit

	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 $\text{Te}(-\text{X})_2$ unit

- Dimers formed by $\text{Te}(-\text{X})_2$ have the same connectivity as those described for $\text{Te}(-\text{X})_1$, *i.e.* two $\text{Te}\cdots\text{X}$ secondary bonds, and the majority are also centrosymmetric. Non centrosymmetric dimers are almost planar in absence of other interactions. Most $\text{X}-\text{Te}\cdots\text{X}$ 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 $\text{Te}(-\text{X})_1$ dimers, where deviation from 90° were present in both directions. Only three dimers of angular $\text{Te}(-\text{X})_2$ were found, centrosymmetric all of them.
- The $\text{Te}(-\text{X})_2$ simple chain is also referable to $\text{Te}(-\text{X})_1$ 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 $\text{Te}(-\text{X})_2$, this would imply the presence of an additional $\text{Te}\cdots\text{X}$ contact leading to a different kind of chain. So, rods in $\text{Te}(-\text{X})_2$ simple chains are equivalent by screw binary axes or by glide planes.
- 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 $\text{Te}\cdots\text{X}$ 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 $\text{X}-\text{Te}-\text{X}$ 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.
- Another finite arrangement of $\text{Te}(-\text{X})_2$ is a cyclic tetramer, where a $\text{Te}(-\text{X})_2$ 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_2X_2 ring are different from the two “terminal” Te atoms placed out of the Te_2X_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.
- Five structures with infrequent spatial groups ($Fdd2$ and $I4_1/acd$) adopt a symmetric polar 3D-network where all secondary bonds are equal. Every $\text{Te}(-\text{X})_2$ rod is bonded to four neighbours, with two bonds from Te and one from every halogen.
 - 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 $\text{Te} \cdots \text{X}$ bonds. Anyway, 4- and 12-membered rings are present.
 - Finally, four pairs of structures were found, each pair with its own arrangement: two chains and two sheets (Figure 7).

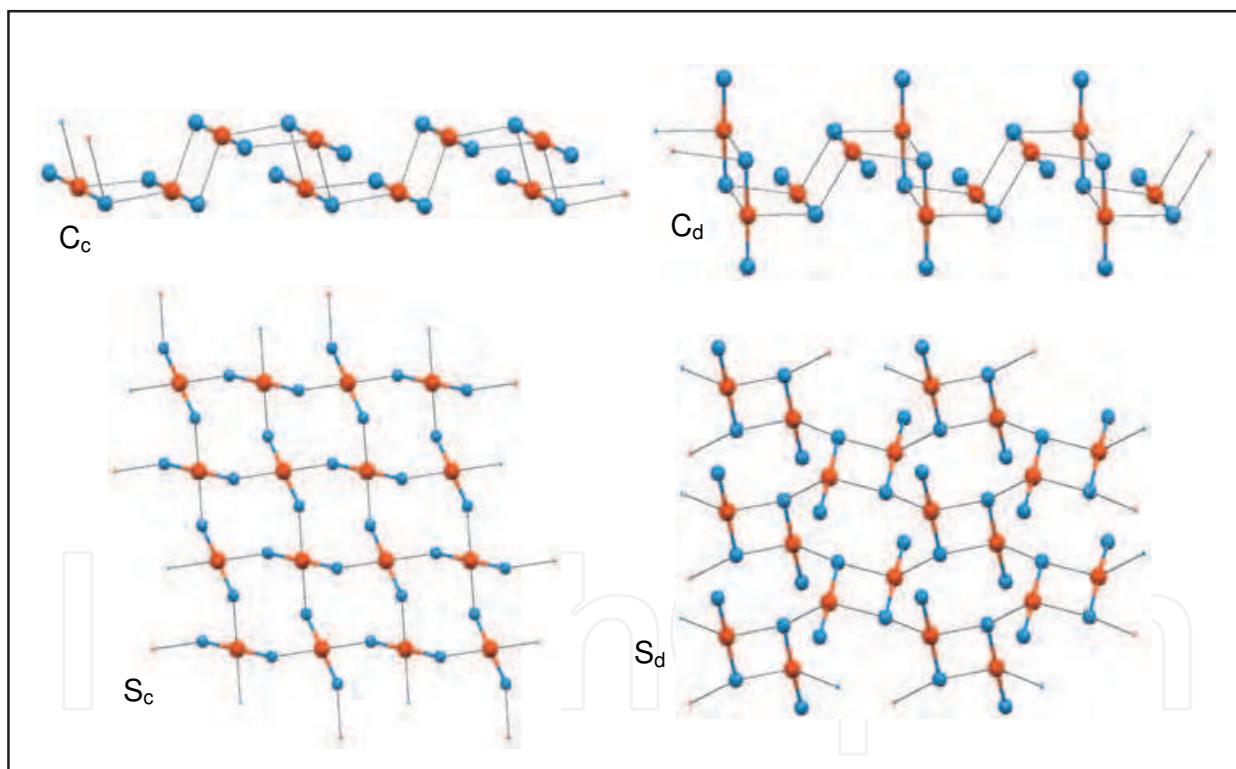


Fig. 7. Less frequent supramolecular arrangements of compounds containing the $\text{Te}(-\text{X})_2$ unit: C_c and C_d chains; S_c and S_d sheets

3.4 Structures of compounds containing the $\text{Te}(-\text{X})_3$ unit

This unit shows a T disposition derived of the tendency of halogen atoms to occupy axial positions (angle $\text{X}-\text{Te}-\text{X}$ 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).

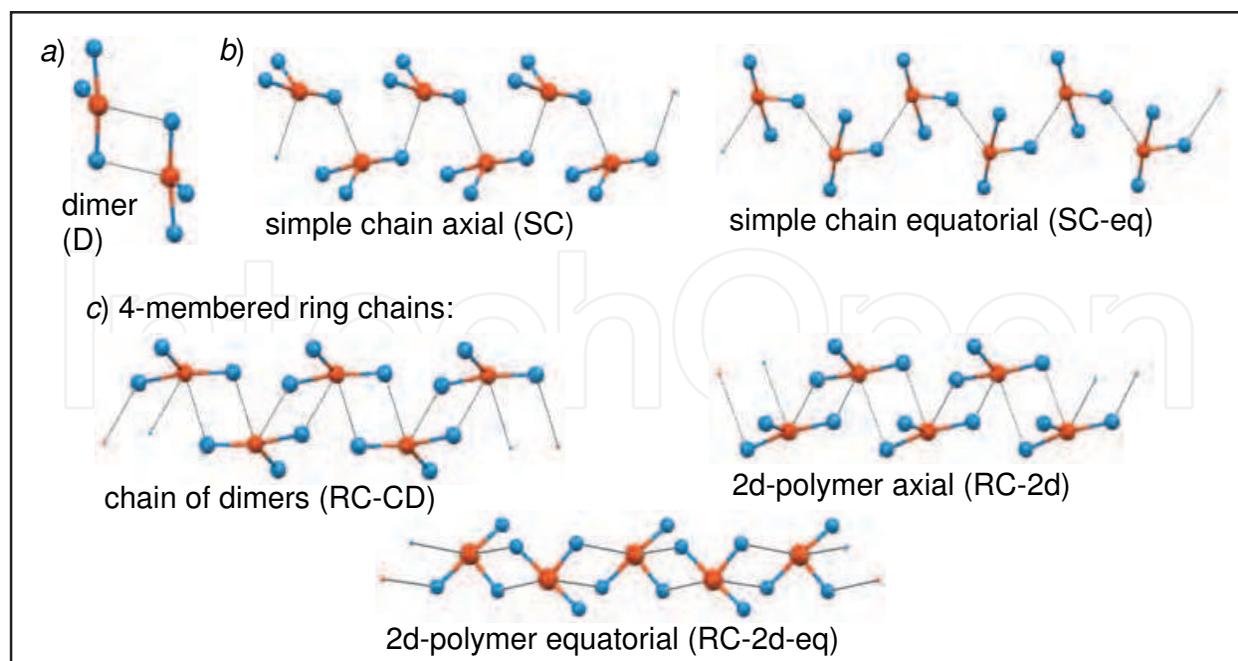


Fig. 8. Main supramolecular arrangements of compounds containing the $\text{Te}(-\text{X})_3$ unit: dimer (D); simple chain involving only axial halogen atoms (SC) or equatorial halogen atoms (SC-eq); 4-membered ring chain: chain of dimers (RC-CD), 2d-polymer involving only axial halogen atoms (RC-2d), 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 $\text{Te}(-\text{X})_3$ unit

- Dimer. As in $\text{Te}(-\text{X})_1$ and $\text{Te}(-\text{X})_2$ 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 $\text{Te}-\text{X}_{\text{eq}}$ bond and the normal to planar core is less than 20° but in three cases this angle is significantly higher, $37-53^\circ$.
- Simple chain. As in $\text{Te}(-\text{X})_1$ and $\text{Te}(-\text{X})_2$ simple chains, two units $\text{Te}(-\text{X})_3$ are linked by one $\text{Te}\cdots\text{X}$ secondary bond. The link involves either axial (3 structures) or equatorial halogen (2 structures). As in $\text{Te}(-\text{X})_2$ chains, units in $\text{Te}(-\text{X})_3$ 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.
- 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 $\text{Te}\cdots\text{X}$ distances (screw binary axis). In the other case, analogous to the $\text{Te}(-\text{X})_2$ 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).

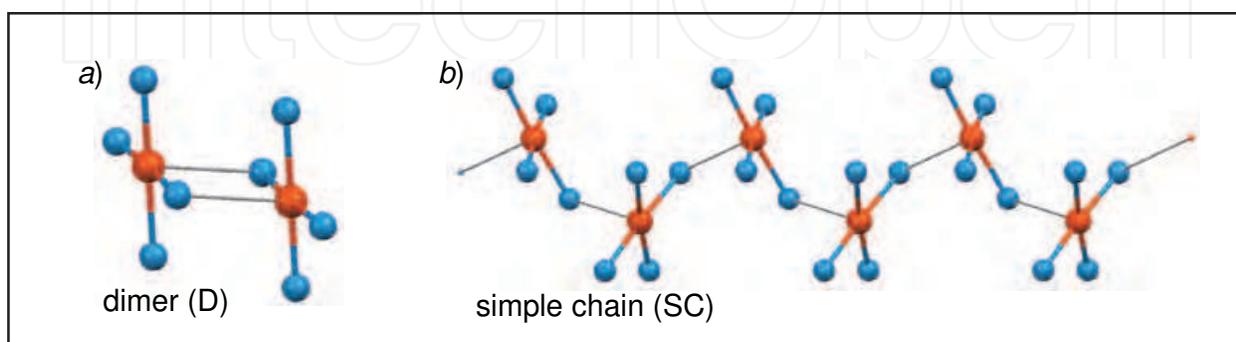


Fig. 9. Main supramolecular arrangements of compounds containing the Te(-X)₄ unit

	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

- 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.
- 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-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.

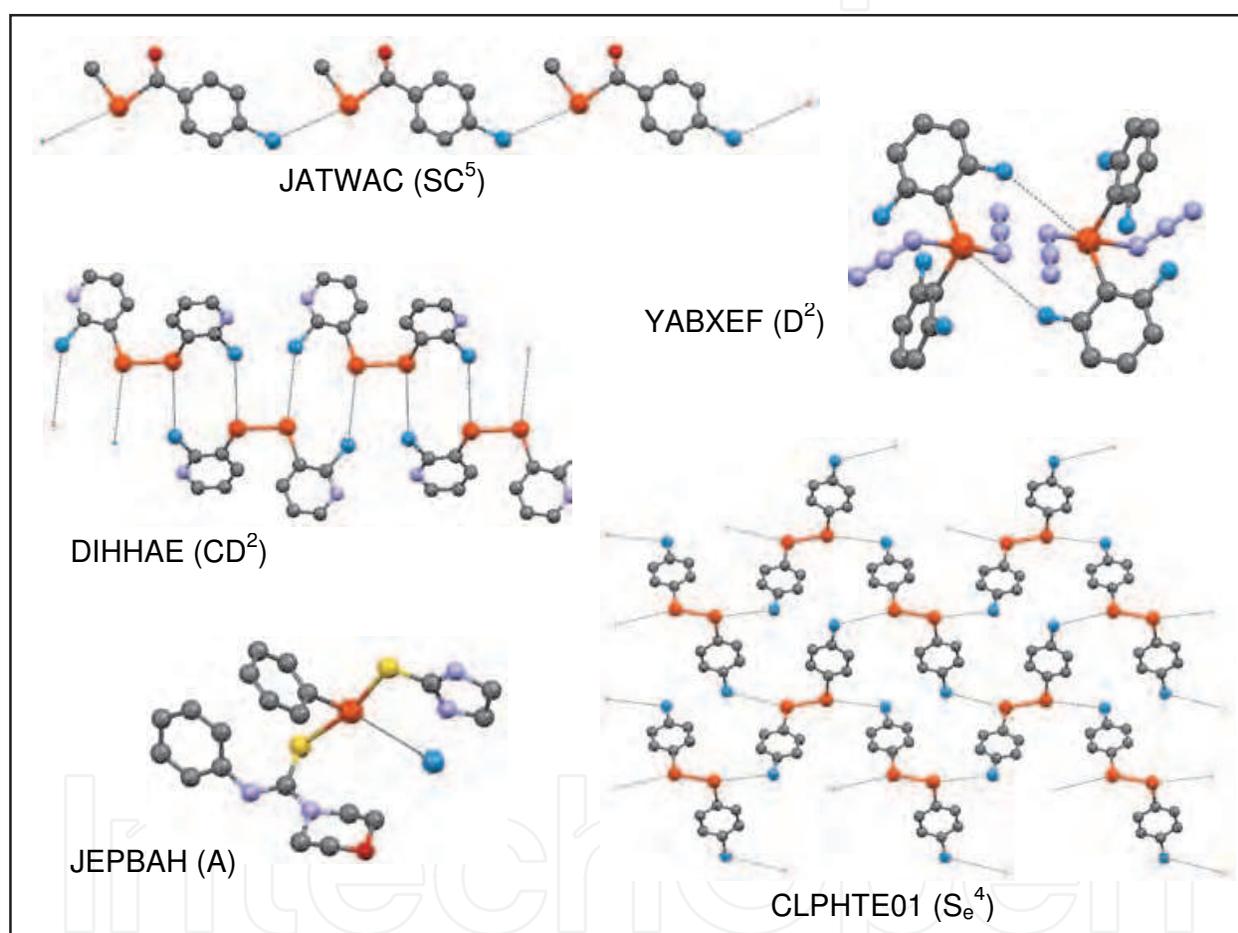


Fig. 10. Examples of supramolecular arrangements in the $\text{Te}(-\text{X})_0$ group: dimer (D); simple chain (SC); chain of dimers (CD); specific sheet (S_e); adduct (A). Superscripts stand for the number of atoms between Te and X atoms

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 $\text{Te}(-\text{X})_1$ group, seven in the $\text{Te}(-\text{X})_2$ group, one in the $\text{Te}(-\text{X})_3$ group, and one in the $\text{Te}(-\text{X})_0$ 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.

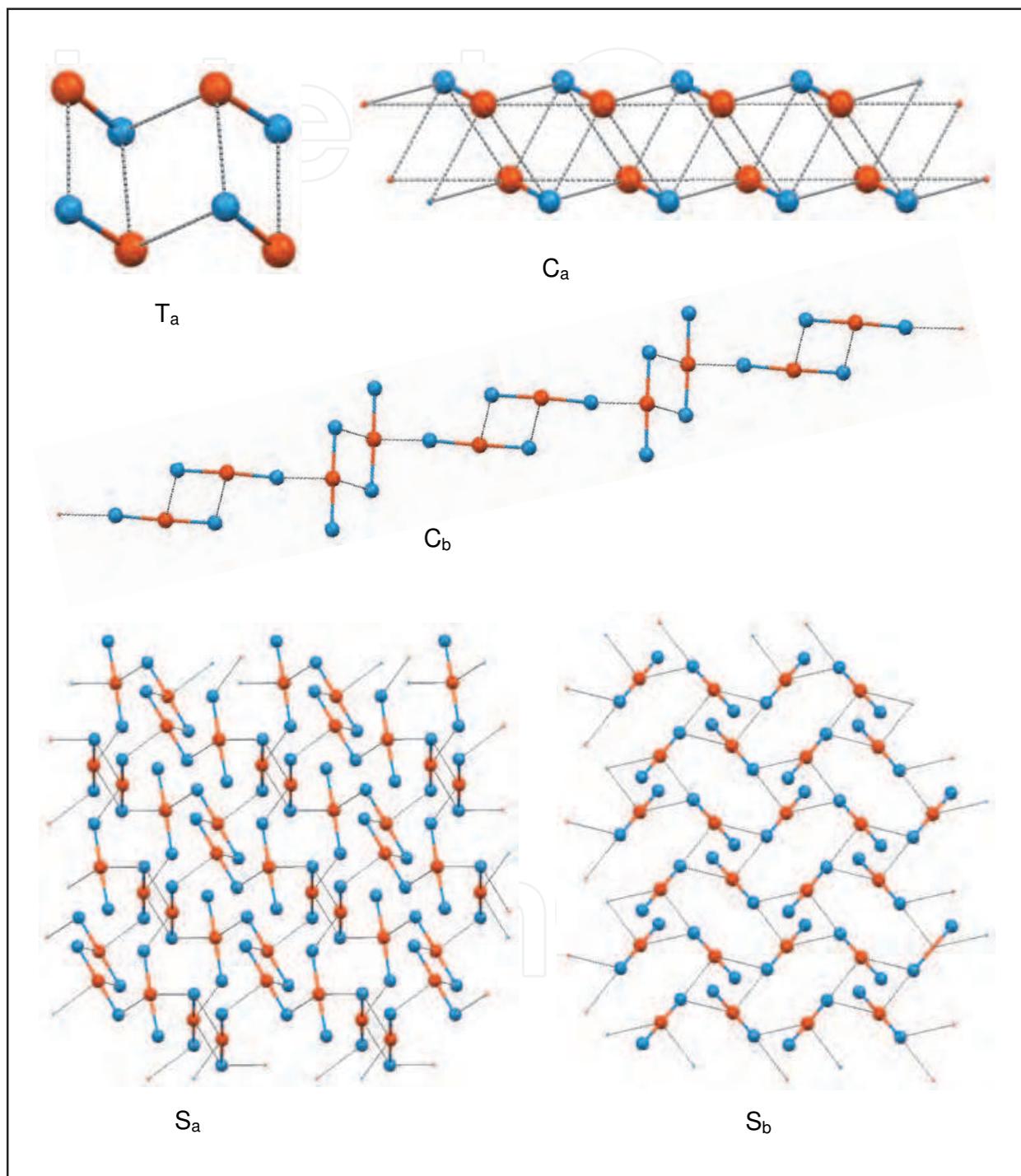


Fig. 11. Some specific arrangements present in polymorphic structures: T_a tetramer; C_a and C_b chains; S_a and S_b sheets

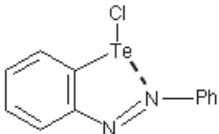
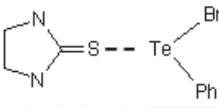
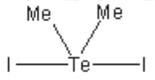
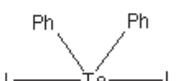
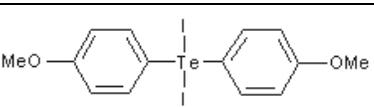
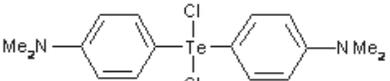
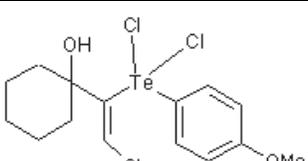
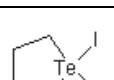
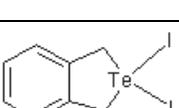
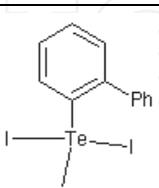
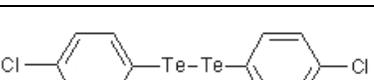
	Refcode	S. G.	Arrang.	D _c (g cm ⁻³)
	PAZPTE PAZPTE01	<i>P</i> -1 <i>I</i> 2/ <i>a</i>	T _a C _a	1.942 1.966
	BTUPTE BTUPTE01	<i>C</i> 2/ <i>c</i> <i>P</i> 2 ₁ / <i>c</i>	0 D	2.106 2.017
	DIDMTE DIDMTE01	<i>P</i> 2 ₁ / <i>c</i> <i>C</i> 2/ <i>c</i>	S _a RC	3.393 3.410
	CIFLEI CIFLEI01	<i>I</i> 4 ₁ <i>P</i> 2 ₁ / <i>c</i>	N C _b	2.556 2.534
	NUNHUZ NUNHUZ01	<i>P</i> -1 <i>P</i> -1	T T	2.256 2.287
	SABCI SABCI01	<i>P</i> <i>n</i> <i>I</i> <i>bca</i>	0 D	1.669 1.666
	ASEHUB ASEHUB01	<i>P</i> 2 ₁ / <i>c</i> <i>P</i> 2 ₁ / <i>a</i>	0 SC	1.759 1.737
	QIXZAY QIXZAY03	<i>P</i> 2 ₁ / <i>n</i> <i>P</i> 2 ₁ / <i>c</i>	C _c C _d	3.138 3.263
	DIBTEP02 DIBTEP10	<i>F</i> <i>dd</i> 2 <i>P</i> 2 ₁ / <i>c</i>	N S _b	2.843 2.887
	BIPTEI BIPTEI01	<i>P</i> 2 ₁ / <i>n</i> <i>P</i> 2 ₁ / <i>c</i>	SC D	2.861 2.777
	CLPHTE CLPHTE01	<i>P</i> 2 ₁ / <i>n</i> <i>P</i> 2 ₁ 2 ₁ 2 ₁	N _a S _e ⁴	2.316 2.365

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_c, C_d: specific chains (Fig. 7); S_e⁴: specific chain (Fig. 10); C_a, C_b, T_a, S_a, S_b: specific chains, tetramer, sheets (Fig. 11); N_a specific 3D-network

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.

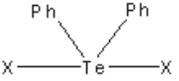
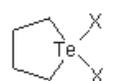
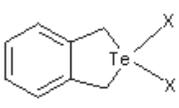
Series	F	Cl	Br	I	
	KEHBIJ S _c	BIBBOE S	BIBCEV C _c	QIXZAY C _c	QIXZAY03 C _d
	GETHOC S _c	BIBCAR N	BIBBUK N	DIBTEP02 N	DIBTEP10 S _b
	FPHTEL RC	OPNTED10 SC	DPHTEB01 N	CIFLEI N	CIFLEI01 C _b

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).

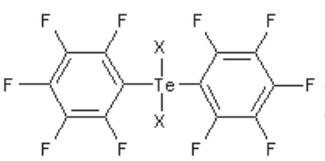
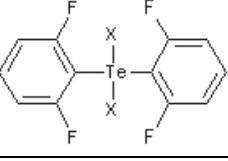
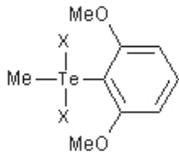
Series	F	Cl	Br	I
		YASVAP RC	YASVET RC	
	IDEXIY RC	IDEXOZ RC		
			TUWPAC RC	TUWPIK RC

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)₁ unit				
<i>a) Dimers</i>				
BSEUTE	<i>Acta Chem.Scand.A</i>	29	763	1975
BTUPTE01	<i>Acta Chem.Scand.A</i>	29	738	1975
BZETBS	<i>Acta Chem.Scand.</i>	20	132	1966
BZETCS	<i>Acta Chem.Scand.</i>	20	132	1966
CEHFAW	<i>Organometallics</i>	18	803	1999
CETUTE	<i>Acta Chem.Scand.A</i>	29	763	1975
DONQEC	<i>Inorg.Chem.</i>	38	3994	1999
DONQIG	<i>Inorg.Chem.</i>	38	3994	1999
DONQOM	<i>Inorg.Chem.</i>	38	3994	1999
ERIBIQ	<i>Organometallics</i>	22	5473	2003
GEDSEO	<i>Z.Kristallogr.</i>	221	166	2006
HIFVOH	<i>Acta Crystallogr.,Sect.C</i>	52	424	1996
OCICIN	<i>Chem.-Eur.J.</i>	12	2515	2006
OLODUO	<i>Acta Crystallogr.,Sect.C</i>	59	o571	2003
OLOFAW	<i>Acta Crystallogr.,Sect.C</i>	59	o571	2003
PETBIA	<i>Z.Anorg.Allg.Chem.</i>	633	127	2007
PETBOG	<i>Z.Anorg.Allg.Chem.</i>	633	127	2007
POYGEP	<i>J.Organomet.Chem.</i>	549	257	1997
POYGIT	<i>J.Organomet.Chem.</i>	549	257	1997
QANWEH	<i>J.Organomet.Chem.</i>	605	39	2000
QIYBAB	<i>J.Organomet.Chem.</i>	623	74	2001
QOKZIZ	<i>Polyhedron</i>	20	203	2001
ROCTAE	<i>Inorg.Chem.</i>	36	1890	1997
TEGZIP	<i>Acta Crystallogr.,Sect.C</i>	52	2022	1996
WEXBIK	<i>Khim.Get.Soedin.,SSSR</i>		417	1994
WOMDIL	<i>Phosphorus,Sulfur,Silicon</i>	123	313	1997
YEXWIH	<i>Inorg.Chem.</i>	33	6154	1994
YEXWON	<i>Inorg.Chem.</i>	33	6154	1994
YEXWUT	<i>Inorg.Chem.</i>	33	6154	1994
<i>Dimers connected by covalent skeleton</i>				
HOJJEV01	<i>Angew.Chem.,Int.Ed.</i>	39	1796	2000
REDXEE	<i>Eur.J.Inorg.Chem.</i>		1294	2006
<i>b) Simple chains</i>				
BRTEBA	<i>Acta Crystallogr.,Sect.B</i>	35	849	1979
CEHKEF	<i>Organometallics</i>	18	803	1999
CIDKOQ	<i>Inorg.Chem.</i>	46	3275	2007
JABWUE	<i>J.Am.Chem.Soc.</i>	110	6762	1988

JEKDAE	<i>Can.J.Chem.</i>	67	1735	1989
KEZMEI	<i>Acta Crystallogr.,Sect.E</i>	63	o1674	2007
MIYPAL	<i>Z.Anorg.Allg.Chem.</i>	628	833	2002
OFUWER	<i>J.Fluorine Chem.</i>	112	207	2001
RIFTAB	<i>Can.J.Chem.</i>	74	1968	1996
RIGKIB	<i>Tetrahedron:Asymm.</i>	7	2797	1996
ROCTEI	<i>Inorg.Chem.</i>	36	1890	1997
TATZAP	<i>Inorg.Chem.</i>	35	2831	1996
ZISWON	<i>Organometallics</i>	14	4755	1995

Structures of compounds containing the Te(-X)₂ unit

a) Dimers

CIDKEG	<i>Inorg.Chem.</i>	46	3275	2007
CLPTEI	<i>Acta Crystallogr.</i>	15	887	1962
DMTEII	<i>Inorg.Chem.</i>	18	311	1979
GACXUD01	<i>Acta Crystallogr.,Sect.C</i>	47	703	1991
GIPRED	<i>Angew.Chem.,Int.Ed.</i>	46	8277	2007
GOKDUG	<i>Z.Kristallogr.</i>	223	536	2008
HEXBOB	<i>Can.J.Chem.</i>	72	1844	1994
HOFKES	<i>Acta Crystallogr.,Sect.C</i>	55	1339	1999
JATSIG	<i>J.Chem.Soc.,Dalton Trans.</i>		1697	1989
KOBYAB	<i>Acta Crystallogr.,Sect.C</i>	47	1858	1991
LAFNUB	<i>Z.Naturforsch.,B:Chem.Sci.</i>	48	199	1993
OCICUZ	<i>Chem.-Eur.J.</i>	12	2515	2006
OFUTOZ	<i>Dalton Trans.</i>		4023	2008
PEKLUM	<i>J.Crystallogr.Spectrosc.Res.</i>	23	181	1993
SABCI01	<i>Acta Crystallogr.,Sect.E</i>	61	o986	2005
SEPMAB	<i>J.Chem.Soc.,Dalton Trans.</i>		907	1990
TUWNOO	<i>Dalton Trans.</i>		973	2003
TUWNUU	<i>Dalton Trans.</i>		973	2003
TUWPEG	<i>Dalton Trans.</i>		973	2003
UJAMIC	<i>J.Organomet.Chem.</i>	695	2532	2010
UJAMUO	<i>J.Organomet.Chem.</i>	695	2532	2010
UJORUH	<i>J.Organomet.Chem.</i>	695	2118	2010
UKAFAO	<i>Inorg.Chem.</i>	49	7577	2010
UKAFES	<i>Inorg.Chem.</i>	49	7577	2010
UKAFIW	<i>Inorg.Chem.</i>	49	7577	2010
UKAFOC	<i>Inorg.Chem.</i>	49	7577	2010
UKAGET	<i>Inorg.Chem.</i>	49	7577	2010
UKAGIX	<i>Inorg.Chem.</i>	49	7577	2010
VOHVET	<i>J.Organomet.Chem.</i>	418	339	1991
WECQIF	<i>Z.Anorg.Allg.Chem.</i>	632	659	2006
WECQOL	<i>Z.Anorg.Allg.Chem.</i>	632	659	2006
WIDZOZ	<i>Z.Anorg.Allg.Chem.</i>	633	1261	2007

WIDZUF	<i>Z.Anorg.Allg.Chem.</i>	633	1261	2007
XAWNUF	<i>Z.Anorg.Allg.Chem.</i>	631	2677	2005
XEXJAM	<i>J.Organomet.Chem.</i>	691	5867	2006
XEXKUH	<i>J.Organomet.Chem.</i>	691	5887	2006
XOTBIS	<i>J.Organomet.Chem.</i>	694	1557	2009
YEZXEH	<i>Organometallics</i>	26	1955	2007
ZARCIE	<i>Can.J.Chem.</i>	73	255	1995
b) Simple chains				
ASEHUB01	<i>Z.Kristallogr.</i>	218	636	2003
BOQJIA	<i>Acta Crystallogr.,Sect.C</i>	55	1930	1999
CEDDAQ	<i>J.Org.Chem.</i>	48	5149	1983
CEJPAJ	<i>Heteroat.Chem.</i>	16	316	2005
CLCHTE	<i>Cryst.Struct.Commun.</i>	9	533	1980
GOKFAO	<i>Z.Kristallogr.</i>	223	536	2008
IDEXEU	<i>Inorg.Chem.</i>	40	5169	2001
JILXAD	<i>Acta Crystallogr.,Sect.C</i>	47	960	1991
KAKCOP	<i>Aust.J.Chem.</i>	58	119	2005
KEQCIT	<i>Inorg.Chim.Acta</i>	359	4619	2006
MIDWAY	<i>Struct.Chem.</i>	18	181	2007
NIJQOM	<i>Polyhedron</i>	16	2441	1997
OFUVER	<i>Dalton Trans.</i>		4023	2008
OFUVIV	<i>Dalton Trans.</i>		4023	2008
OPNTED10	<i>J.Chem.Soc.,Dalton Trans.</i>		251	1982
QOGPAD	<i>Acta Crystallogr.,Sect.C</i>	57	749	2001
SEJPIG	<i>Acta Crystallogr.,Sect.C</i>	46	251	1990
STECHB	<i>Inorg.Chem.</i>	11	3026	1972
TLCLTE	<i>Cryst.Struct.Commun.</i>	9	539	1980
UJOSAO	<i>J.Organomet.Chem.</i>	695	2118	2010
UJOSOC	<i>J.Organomet.Chem.</i>	695	2118	2010
VUZJIJ	<i>Acta Crystallogr.,Sect.C</i>	44	2182	1988
XUCNIS	<i>Chin.J.Chem.</i>	19	457	2001
XUCNOY	<i>Chin.J.Chem.</i>	19	457	2001
XURRAE	<i>Dalton Trans.</i>	39	2637	2010
XURSEJ	<i>Dalton Trans.</i>	39	2637	2010
YOWMEC	<i>Acta Crystallogr.,Sect.C</i>	51	861	1995
YUFNUI	<i>Z.Kristallogr.</i>	210	306	1995
c) Chains of 4-membered rings				
BZTELI10	<i>Inorg.Chem.</i>	14	1142	1975
CEGNOR	<i>J.Chem.Soc.,Dalton Trans.</i>		23	1984
HIQSUV	<i>Acta Crystallogr.,Sect.C</i>	55	648	1999
IDEXIY	<i>Inorg.Chem.</i>	40	5169	2001
PTELDI10	<i>Inorg.Chem.</i>	12	2669	1973
YASVAP	<i>Z.Anorg.Allg.Chem.</i>	619	1269	1993
YASVET	<i>Z.Anorg.Allg.Chem.</i>	619	1269	1993

IDEXO	<i>Inorg.Chem.</i>	40	5169	2001
IDEXUK	<i>Inorg.Chem.</i>	40	5169	2001
LEVKED	<i>J.Am.Chem.Soc.</i>	128	14949	2006
MIHFIS	<i>J.Fluorine Chem.</i>	102	301	2000
TUWNII	<i>Dalton Trans.</i>		973	2003
TUWPAC	<i>Dalton Trans.</i>		973	2003
TUWPIK	<i>Dalton Trans.</i>		973	2003
UKAFUI	<i>Inorg.Chem.</i>	49	7577	2010
UKAGAP	<i>Inorg.Chem.</i>	49	7577	2010
VOTSIG	<i>Organometallics</i>	11	954	1992
XUPXAI	<i>Heterocycles</i>	80	1339	2010
CERWIF	<i>J.Organomet.Chem.</i>	262	151	1984
COBPOY	<i>J.Organomet.Chem.</i>	268	141	1984
DIDMTE01	<i>Dalton Trans.</i>		6274	2008
FPHTEL	<i>J.Chem.Soc.,Dalton Trans.</i>		2306	1980
MIHFEO	<i>J.Fluorine Chem.</i>	102	301	2000
YUPHIB	<i>Z.Anorg.Allg.Chem.</i>	635	862	2009
d) Tetramers				
BOHNAN	<i>Acta Crystallogr.,Sect.C</i>	39	45	1983
BUNDIY	<i>Inorg.Chem.</i>	48	10330	2009
CIMFOT	<i>Acta Crystallogr.,Sect.C</i>	40	1349	1984
IHOFIU	<i>J.Organomet.Chem.</i>	669	149	2003
LIMZEM	<i>Acta Crystallogr.,Sect.C</i>	51	639	1995
NUNHUZ	<i>Acta Crystallogr.,Sect.C</i>	54	995	1998
NUNHUZ01	<i>Acta Crystallogr.,Sect.C</i>	54	995	1998
PHTECL	<i>Inorg.Chem.</i>	19	2556	1980
PIXPES	<i>J.Organomet.Chem.</i>	693	957	2008
e) Sheets				
BIBBOE	<i>Polyhedron</i>	23	1629	2004
LUTBUX	<i>Can.J.Chem.</i>	80	1530	2002
OTEHEX	<i>Inorg.Chem.</i>	12	2665	1973
VIVGEM	<i>J.Organomet.Chem.</i>	410	309	1991
f) 3D-Networks				
BIBBUK	<i>Polyhedron</i>	23	1629	2004
BIBCAR	<i>Polyhedron</i>	23	1629	2004
CIFLEI	<i>J.Chem.Soc.,Dalton Trans.</i>		869	1984
DIBTEP02	<i>Inorg.Chem.</i>	24	1814	1985
DPHTEB01	<i>Acta Crystallogr.,Sect.E</i>	60	o2511	2004
g) Less frequent arrangements				
BIBCEV	<i>Polyhedron</i>	23	1629	2004
QIXZAY	<i>J.Organomet.Chem.</i>	623	74	2001
QIXZAY03	<i>Inorg.Chem.</i>	43	3742	2004
SIDGIW	<i>Struct.Chem.</i>	18	223	2007
COQNOL01	<i>Inorg.Chem.</i>	38	3994	1999

DMTECL01	<i>J.Am.Chem.Soc.</i>	105	229	1983
GETHOC	<i>J.Organomet.Chem.</i>	349	95	1988
KEHBIJ	<i>Z.Naturforsch.,B:Chem.Sci.</i>	61	528	2006

Structures of compounds containing the Te(-X)₃ unit

a) Dimers

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

b) Simple chains

BONHUH	<i>Cryst.Struct.Commun.</i>	11	1593	1982
DOTLUT	<i>J.Org.Chem.</i>	51	1692	1986
PAFLIR	<i>Inorg.Chem.</i>	31	1431	1992
BIPTEI	<i>Inorg.Chem.</i>	15	2728	1976
UDUHUW	<i>Organometallics</i>	21	526	2002

c) Chains of 4-membered rings

WEQVET	<i>J.Organomet.Chem.</i>	598	49	2000
MUWBIP	<i>J.Organomet.Chem.</i>	664	306	2002
OLODOI	<i>Acta Crystallogr.,Sect.C</i>	59	o571	2003
WERWUM	<i>J.Organomet.Chem.</i>	691	4807	2006
YIHRAJ	<i>Z.Anorg.Allg.Chem.</i>	633	1618	2007

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

a) Dimers

CIFVOD	<i>J.Organomet.Chem.</i>	692	3081	2007
CIFVUJ	<i>J.Organomet.Chem.</i>	692	3081	2007
CIFWAQ	<i>J.Organomet.Chem.</i>	692	3081	2007
CITMAT	<i>Tetrahedron</i>	40	1607	1984
CUCGOW	<i>Can.J.Chem.</i>	62	32	1984
DEBXOY	<i>Appl.Organomet.Chem.</i>	19	1196	2005
DEBXUE	<i>Appl.Organomet.Chem.</i>	19	1196	2005

ELAVAP	<i>Inorg.Chim.Acta</i>	365	492	2011
IHIMAO	<i>J.Organomet.Chem.</i>	694	2463	2009
IHIMES	<i>J.Organomet.Chem.</i>	694	2463	2009
JASCAI	<i>Z.Anorg.Allg.Chem.</i>	631	1524	2005
MECGEH	<i>Eur.J.Inorg.Chem.</i>		958	2006
MECGOR	<i>Eur.J.Inorg.Chem.</i>		958	2006
MTEMTE	<i>J.Chem.Soc.A</i>		2018	1967
WUGVUQ	<i>J.Braz.Chem.Soc.</i>	17	1566	2006
WUTJOK	<i>Z.Anorg.Allg.Chem.</i>	629	215	2003
b) Simple chains				
IJOHUK	<i>Inorg.Chem.Commun.</i>	6	869	2003
IJOJAS	<i>Inorg.Chem.Commun.</i>	6	869	2003
JASBUB	<i>Z.Anorg.Allg.Chem.</i>	631	1524	2005
KEQCAL	<i>Inorg.Chim.Acta</i>	359	4619	2006
MECGUX	<i>Eur.J.Inorg.Chem.</i>		958	2006
WUGVIE	<i>J.Braz.Chem.Soc.</i>	17	1566	2006
WUGVOK	<i>J.Braz.Chem.Soc.</i>	17	1566	2006

Structures of compounds without Te-X units [Te(-X)₀] in Figure

CLPHTE01	<i>Acta Crystallogr.,Sect.C</i>	40	1011	1984
DIHHAE	<i>Bioinorg.Chem.Appl.</i>		69263	2007
JATWAC	<i>Inorg.Chem.</i>	38	519	1999
JEPBAH	<i>Acta Chem.Scand.</i>	44	464	1990
YABXEF	<i>J.Fluorine Chem.</i>	125	997	2004

Polymorphs

ASEHUB	<i>Z.Kristallogr.</i>	218	636	2003
ASEHUB01	<i>Z.Kristallogr.</i>	218	636	2003
BIPTEI	<i>Inorg.Chem.</i>	15	2728	1976
BIPTEI01	<i>Inorg.Chem.</i>	16	2318	1977
BTUPTE	<i>Acta Chem.Scand.A</i>	29	738	1975
BTUPTE01	<i>Acta Chem.Scand.A</i>	29	738	1975
CIFLEI	<i>J.Chem.Soc.,Dalton Trans.</i>		869	1984
CIFLEI01	<i>J.Chem.Soc.,Dalton Trans.</i>		869	1984
CLPHTE	<i>Acta Crystallogr</i>	10	201	1957
CLPHTE01	<i>Acta Crystallogr.,Sect.C</i>	40	1011	1984
DIBTEP10	<i>J.Organomet.Chem.</i>	178	423	1979
DIDMTE	<i>J.Chem.Soc.,Dalton Trans.</i>		316	1972
DIDMTE01	<i>Dalton Trans.</i>		6274	2008
NUNHUZ	<i>Acta Crystallogr.,Sect.C</i>	54	995	1998
NUNHUZ01	<i>Acta Crystallogr.,Sect.C</i>	54	995	1998
PAZPTE	<i>J.Chem.Res.</i>	145	1901	1979
PAZPTE01	<i>J.Organomet.Chem.</i>	549	257	1997
QIXZAY	<i>J.Organomet.Chem.</i>	623	74	2001

QIXZAY03	<i>Inorg.Chem.</i>	43	3742	2004
SABCII	<i>Inorg.Chem.</i>	43	4106	2004
SABCII01	<i>Acta Crystallogr.,Sect.E</i>	61	o986	2005
Halogen series				
KEHBIJ	<i>Z.Naturforsch.,B:Chem.Sci.</i>	61	528	2006
BIBBOE	<i>Polyhedron</i>	23	1629	2004
BIBCEV	<i>Polyhedron</i>	23	1629	2004
QIXZAY	<i>J.Organomet.Chem.</i>	623	74	2001
QIXZAY03	<i>Inorg.Chem.</i>	43	3742	2004
GETHOC	<i>J.Organomet.Chem.</i>	349	95	1988
BIBCAR	<i>Polyhedron</i>	23	1629	2004
BIBBUK	<i>Polyhedron</i>	23	1629	2004
DIBTEP02	<i>Inorg.Chem.</i>	24	1814	1985
DIBTEP10	<i>J.Organomet.Chem.</i>	178	423	1979
FPHTEL	<i>J.Chem.Soc.,Dalton Trans.</i>		2306	1980
OPNTED10	<i>J.Chem.Soc.,Dalton Trans.</i>		251	1982
DPHTEB01	<i>Acta Crystallogr.,Sect.E</i>	60	o2511	2004
CIFLEI	<i>J.Chem.Soc.,Dalton Trans.</i>		869	1984
CIFLEI01	<i>J.Chem.Soc.,Dalton Trans.</i>		869	1984
YASVAP	<i>Z.Anorg.Allg.Chem.</i>	619	1269	1993
YASVET	<i>Z.Anorg.Allg.Chem.</i>	619	1269	1993
IDEXO	<i>Inorg.Chem.</i>	40	5169	2001
IDEXIY	<i>Inorg.Chem.</i>	40	5169	2001
TUWPAC	<i>Dalton Trans.</i>		973	2003
TUWPIK	<i>Dalton Trans.</i>		973	2003

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.

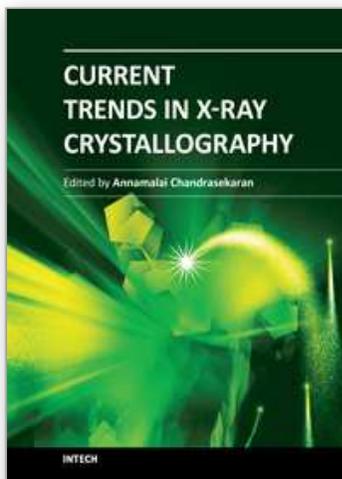
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