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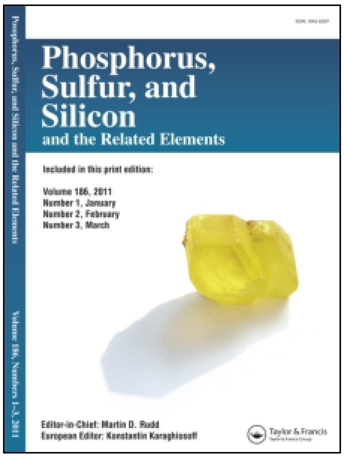

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Diorganotellurium(IV) Dihalides and Secondary Bonding: Revisiting the Coordination Polyhedra

Julio Zukerman-schpector[a]; Ionel Haiduc[b]
[a] Departamento de Quimica, Universidade Federal de Sao Carlos, Sao Carlos, SP, Brazil [b] Facultatea de Chimie, Universitatea "Babes-Bolyai", Cluj-Napoca, Roumania

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Diorganotellurium(IV) Dihalides and Secondary Bonding: Revisiting the Coordination Polyhedra

JULIO ZUKERMAN-SCHPECTOR[a] and IONEL HAIDUC[b]

[a]*Departamento de Quimica, Universidade Federal de Sao Carlos, Caixa postal 676, 13565-905 Sao Carlos, SP-Brazil and* [b]*Facultatea de Chimie, Universitatea "Babes-Bolyai", RO-3400 Cluj-Napoca, Roumania*

The coordination geometry of the central atom in diorganotellurium(IV) halides, almost invariably described as ψ-trigonal bipyramidal, is in fact much more diversified. If intra and intermolecular secondary bonds and electron lone pairs are considered ψ-trigonal bipyramidal, ψ-octahedral, ψ-pentagonal bipyramidal and some others coordination geometries can be identified. A careful reexamination of a number of published structures is presented, with the analysis of the coordination polyhedra.

Keywords: coordination polyhedra; secondary bonds; organotellurium(IV) halides; lone pair

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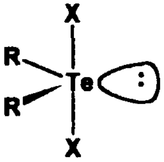
I. INTRODUCTION

Tellurium displays various oxidation states (-II, +II, +IV and +VI) and coordination numbers (CN from 2 to 8) which leads to a variety of compositions and structures. Organotellurium compounds are known which contain from one to six Te-C bonds. The organotellurium halides, containing both Te-C and Te-X bonds (X = halogen) are an important class of compounds of intrinsic interest and important as starting materials for the synthesis of all other functional derivatives. Among these, the diorganotellurium(IV) dihalides, R_2TeX_2, deserve a particular attention. This seems to be the most extensive class of organotellurium halides, easily prepared and well structurally characterized through numerous X-ray structure determinations. Their structure variations will be discussed in this review.

Tellurium(IV) uses four valence electrons to form four sigma bonds (Te-C and Te-X in organotellurium halides) and maintains a lone pair. This implies the use of four bonding orbitals (5s and 5p) to form the four bonds and a fifth valence orbital is required to accommodate the lone pair. In the literature, the bonding in Te(IV) compounds has been described as involving either an sp^3d hybridization or three center-four electron bonds (a model which avoids the use of outer 5d orbitals). The Valence Shell Electron Pair Repulsion Theory (VSEPR)[1] avoids this dilemma by simply considering the geometries determined by the repulsion of electron bonding pairs and lone pairs of the central atom.

The structures of diorganotellurium(IV) dihalides are almost invariably described in the literature as pseudo-trigonal bipyramidal (**1**), with the halogen atoms in axial positions and the organic groups, R, in equatorial positions. The presence of a stereochemically active lone pair, is frequently assumed to occupy an equatorial site.



(1)

This description is in agreement with the VSEPR theory, but it is only a first approximation, valid if only the primary (normal covalent) bonds are considered. In all but few cases, this ideal coordination geometry is altered by the presence of additional secondary bonds to tellurium, which can be due to *intermolecular interactions* with the halogen, oxygen or other donor atoms of adjacent molecules, leading to supramolecular self-assembly,[2] or to *intramolecular interactions* with appropriately located donor atoms in some functional organic groups attached to tellurium. This increases the real coordination number of the central atom. The presence of a stereochemically active lone pair is also quite frequent, as suggested by some apparently empty spaces on the side opposite to the two Te-C bonds, approximately in the equatorial plane. In rare cases of higher coordination polyhedra the lone pair is more difficult to locate.

If a "point-on-a-sphere" model is assummed to describe the geometry of an ideal coordination polyhedron, two types of distortions can be noted: a) an *angular distortion*, *i.e.* a modification of the bond angles, and b) a *radial distortion*, *i.e.* differing interatomic distances between the central atom and the surrounding atoms of the ligands (or

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substituents). The *angular distortion* may be caused by interligand repulsions, by the incorporation of the central atom as heteroatom in a ring, or by much differing sizes of the ligands. The *radial distortion* can be caused by differing atomic radii of the ligating atoms of the substituents and/or by the differing nature of the bonds between the central atom and the substituents (e.g. covalent and secondary bonds between Te and X in our case). These two effects combined may result in real coordination geometries very much differing from those of ideal polyhedra. The coordination polyhedron is no more inscriptible in a sphere and an ovoidal description of the environment seems sometimes more appropriate. Such distorted polyhedra can only approximately be described, sometimes with great difficulty. In tellurium(IV) compounds containing a TeC_2X_2 core of primary bonds, different C-Te-C bond angles should be expected and are indeed observed when the carbon atoms belong to simple alkyl or aryl groups (1) and when are part of five- or six- membered heterocycles, (2) and (3) respectively.

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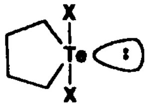

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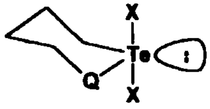

(3)

As mentioned above, in organotellurium halides, intermolecular secondary bonds are observed between the donor atoms of a molecule and the central tellurium atom of an adjacent molecule. The *secondary bond* concept has been introduced by Alcock[3] to describe interatomic distances intermediate between the covalent bond lengths and Van der Waals distances. Their theoretical treatment is not yet fully developed,

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but this type of interactions is explained in terms of three-center four electron bonds[4] and a structural similarity between the secondary bonds and hydrogen bonds has been suggested.

In the forthcoming discussion the following notation will be used: R - organic group; X - halogen atom bonded covalently (i.e. through a *primary bond*) to tellurium; Y - halogen or other donor atom bonded through a *secondary bond*; E - lone pair. Taking into account the additional secondary interactions, the following types of diorganotellurium(IV) dihalide structures are in principle possible, if the lone pair is stereochemically active and its position is included in the coordination number):

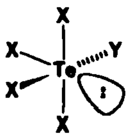
a) R_2TeX_2E-type: no secondary bonds, coordination number 5, ψ-trigonal bipyramidal geometry (**1**);

b) R_2TeX_2YE-type: one secondary bond, coordination number 6, ψ-octahedral geometry (**4**);

c) $R_2TeX_2Y_2E$-type: two secondary bonds, coordination number 7, ψ-pentagonal bipyramidal geometry (**5**); or monocapped octahedron;

d) $R_2TeX_2Y_3E$-type: three secondary bonds, coordination number 8, capped ψ-pentagonal bipyramid (**6**).

e) Other types, e.g. $R_2TeX_2Y_2Z_2E$, with higher coordination numbers, distorted square antiprism, capped pentagonal bipyramid (lone pair not localized).



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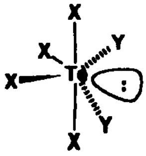

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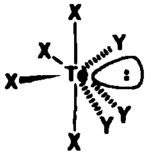

(6)

The number of examples known for each type varies, and the most frequent seems to be the $R_2TeX_2Y_2E$-type.

2. FIVE-COORDINATE, ψ-TRIGONAL BIPYRAMIDAL COMPOUNDS OF R_2TEX_2E-TYPE COMPOUNDS

Five-coordination in diorganotellurium(IV) dihalide is rare. It seems to be limited to cases when the two organic groups attached to tellurium are bulky and crowd the environment arround the central atom. An illustrative example is dichloro[(2-phenyl-tellurophene-3-yl)](4'-phenylbut-3'-yn-1'-enyl)tellurium(IV)(7).[5] In this compound the bulky organic groups protect the tellurium(IV) site and prevent any intermolecular interactions. The Te-Cl bond lengths are basically identic. There are no secondary bonds within the sum of Van der Waals radii plus 10 % around tellurium(IV).

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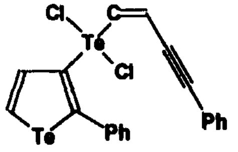

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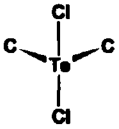

Te-C	2.090 A	2.107 A
Te-Cl	2.501 A	2.512 A
C-Te-C	99.3°	
Cl-Te-Cl	173.93°	
C-Te-Cl (ax/eq)	83.1-91.6°	

The molecular structure shown in FIGURE 1 clearly illustrates the crowded environment around theTe(IV) atom which prevents further interactions. The coordination polyhedron is shown in FIGURE 1b.

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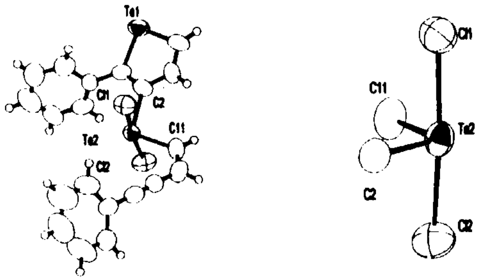
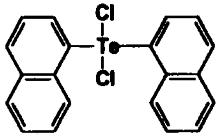


FIGURE 1. Left the molecular structure of (7); right: the coordination polyhedron in (7) (ψ-trigonal pyramidal geometry)

Another example of ψ-trigonal pyramidal five-coordinated tellurium is found in dichloro-bis(1-naphtyl)tellurium(IV) (8).[6]



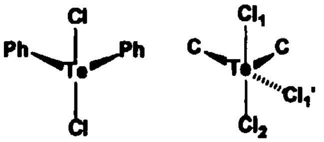
(8)

Te-Cl 2.5603 A   Te-C 2.103 A
Cl-Te-Cl 180°
C-Te-C 100.45°
C-Te-Cl ax/eq 87.7° and 91.9°

Obviously, the voluminous organic groups around tellurium prevent further interactions with the central atom.

3. SIX-COORDINATE, ψ -OCTAHEDRAL COMPOUNDS OF R_2TEX_2YE-TYPE COMPOUNDS

This type of coordinaton geometry is illustrated by the structure of Ph_2TeCl_2 (9)[7], with the coordination polyhedron shown in FIGURE 2. Note the elongated Te···Cl(1)' interatomic distance and the empty space in the equatorial plane, occupied by the lone pair.



(10)

Te-Cl$_1$	2.529 A	Te-Cl$_2$	2.482 A
Te···Cl$_1$'	3.677 A		
Te-C	2.102 and 2.111 A		

Cl$_1$-Te-Cl$_2$	175.54°
C-Te-C	99.0°
C-Te-Cl (ax/eq)	88.06-89.21°
Cl$_1$-Te...Cl$_1$'	85.47°
Cl$_2$-Te...Cl$_1$	98.63°
C-Te...Cl$_1$' cis	95.47°
C-Te...Cl$_1$' trans	164.13°

The tellurium atom forms two equatorial covalent Te-C bonds, two axial covalent Te-Cl bonds and one secondary Te···Cl(1)' bond in the equatorial plane. The Cl(1)' atom belongs to a symmetry related molecule, and the result is the formation of a chain structure based upon a Cl-Te···Cl'-Te'··· alternation. The wide C(1)-Te···Cl' angle of 164.13° in the equatorial plane suggests the presence of a lone pair in this region. The coordination geometry thus becomes ψ-octahedral (5). All other bond angles are close to 90° indicating that the angular distortions of the octahedron are not severe. The major distortion is radial, which is due to the non-equivalence of the tellurium-chlorine bonds. Note that the primary Te-Cl bonds are non-equivalent; the Te-Cl(1) bond which participates in secondary bonding (bridging) is slightly elongated (2.529 Å) compared with the terminal (non-bridging) Te-Cl(2) bond (2.482 Å).

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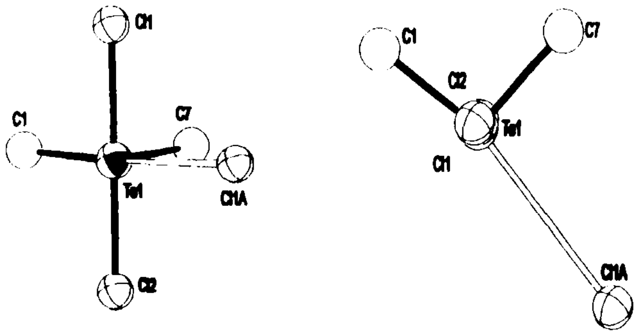

FIGURE 2. The coordination polyhedron in Ph_2TeCl_2. Left: vertical view; right: view down the axial bonds.

Other examples are: β-Ph_2TeI_2,[8] (p-$PhOC_6H_4)_2TeCl_2$ dimer[9] and dibromo(p-dimethylaminophenyl)di-*tert*-butyl-tellurapyrylium tribromide.[10] The main features of the geometry described above are observed in all examples.

In β-Ph_2TeI_2 there are two independent molecules. One of them [Te(1)] contains six-coordinate tellurium displaying an octahedral geometry, with ample space in the equatorial plane for the lone pair (FIGURE 3).[8]

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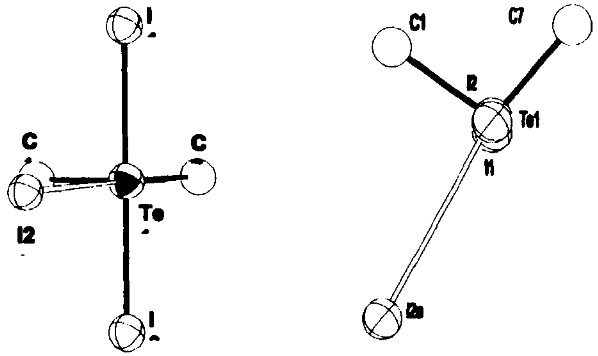

FIGURE 3. The coordination polyhedron in β-Ph$_2$TeI$_2$. Left:vertical view; right: view down the axial bonds.

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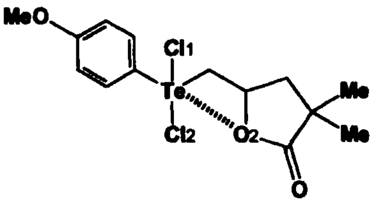
In dichloro[(4,4-dimethyl-5-oxo-2,3,4,5-tetrahydro-2-furyl) methyl](4-methoxy-phenyl)tellurium(IV)[11] the ψ-octahedral geometry is achieved through an *intra*molecular Te···O secondary bond (3.194 Å) and no secondary Te···Cl interactions are present, as the shortest non-bonded tellurium-chlorine distance is 4.956 Å, well beyond the Van der Waals distance. The coordination polyhedron is shown in FIGURE 4.



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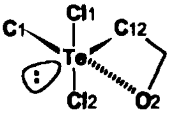

Te-Cl_1	2.490 A	Te-Cl_2	2.507 A;
Te-C_1	2.094 A	Te-C_{12}	2.119 A
Te···O_2	3.194 A		
Cl_1-Te-Cl_2	174.97 °	C_1-Te-C_{12}	98.30°
C-Te-Cl ax/eq	87.1-89.3 °		
Cl_1-Te···O_2	77.24 °	Cl_2-Te···O_2	101.57°
C_1-Te···O_2	143.21 °	C_{12}-Te···O_2	48.05°

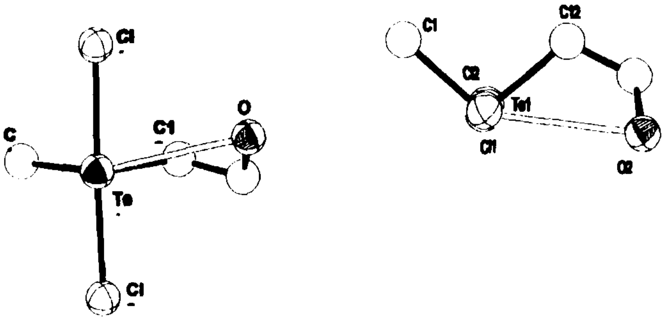

FIGURE 4. The coordination polyhedron in (11). Left: vertical view; right: view down the axial bonds.

It is not clear why a closely structurally related compound cited below, displays a different coordination geometry due to an intermolecular Te···Cl secondary interaction.

4. SEVEN-COORDINATE, ψ-PENTAGONAL BIPYRAMIDAL COMPOUNDS OF $R_2TEX_2Y_2E$-TYPE COMPOUNDS

4.1. Intermolecular Te···X secondary bonds

The seven-coordinate, ψ-pentagonal bipyramidal geometry (6) is

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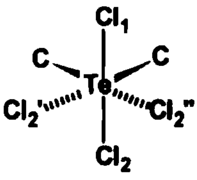
the most common in $R_2TeX_2Y_2E$-type compounds. The protoype is the structure of Me_2TeCl_2,[12,13], and is also found in α-Me_2TeI_2,[14] Me_2TeBr_2,[15] Ph_2TeF_2,[16] Ph_2TeBr_2,[17] Ph_2TeI_2,[18] dichloro(*n*-butyl)(phenylethynyl)tellurium(IV), $Bu(PhCC)TeCl_2$,[19] $(4\text{-}BrC_6H_4)Ph$ $TeCl_2$,[20] $(4\text{-}BrC_6H_4)_2TeCl_2$,[21] $(4\text{-}MeOC_6H_4)_2TeCl_2$,[22] $(C_6F_5)_2TeX_2$ (X = Cl, Br),[23] 3,4-benzo-1-telluracyclopentane diiodide, $C_6H_4(CH_2)_2$ TeI_2,[24] dibenzotellurophene diiodide,[25] phenoxatellurin 10,10-dichloride $O(C_6H_4)_2TeCl_2$,[26] phenoxatellurin 10,10-diiodide $O(C_6H_4)_2$ TeI_2,[27] 1-oxa-4-telluracyclohexane4,4-diiodide $O(CH_2CH_2)_2TeI_2$,[28] dichloro(2',4'-dimethoxyphenyl(trans-6-oxabicyclo[3.2.1]oct-4-yl) tellurium(IV)[29], dichloro(4-methoxyphenyl)(2-oxocyclohexyl) tellurium(IV),[30] $(Cl_2Ph)TeCH_2Te(PhCl_2)$,[31] 1,1,5,5,9,9-hexachloro-1,5,9-tritelluracyclododecane[32] and other compounds. We will discuss first the prototype.

In Me_2TeCl_2[32] the tellurium atom is surrounded by two equatorial Te-C bonds, two axial Te-Cl bonds and two equatorial secondary Te···Cl bonds; the enlarged Cl'···Te-Cl" angle of 108.30° suggests the presence of the lone pair also in the equatorial plane or in its vicinity. This leads to a distorted ψ-pentagonal bipyramidal geometry, with the two chlorine atoms [Cl(1) and Cl(2)] in axial positions and all other bonds in equatorial positions. The two secondary bonded Cl(2A) and Cl(2B) belong to two different neighbouring molecules of a supramolecular double chain structure. The coordination polyhedron of Me_2TeCl_2 is illustrated in FIGURE 5.

It can be observed that one of the secondary bonded chlorine atom, Cl(2A) is displaced from the equatorial plane, as demonstrated by the small Cl(2)-Te···Cl(2A) angle of only 74.80°, probably to leave more room for the lone pair in the space of the wide Cl(2A)···Te···Cl(2B) angle of 108.30°. Electron density maps determined by single crystal X-ray diffraction, indeed show a zone of high electron density in the region where the lone pair is expected.



(12)

Te-Cl$_1$	2.488 A	Te-Cl$_2$	2.541 A
Te···Cl$_2$'	3.412 A	Te···Cl$_2$"	3.478 A
Te-C	2.116 and 2.112 A		

C-Te-C	87.66°	Cl$_1$-Te-Cl$_2$	172.44°
C-Te-Cl (ax/eq)	86.50-89.29°		
Cl$_2$'···Te···Cl$_2$"	108.30°	Cl$_1$-Te···Cl$_2$'	93.39°
Cl$_1$···Te···Cl$_2$"	109.04°		
Cl$_2$-Te···Cl$_2$'	91.47°	Cl$_2$-Te···Cl$_2$"	74.80°
C-Te···Cl$_2$' cis	72.80°	C-Te···Cl$_2$' trans	169.35°
C-Te···Cl$_2$" cis	81.27°	C-Te···Cl$_2$" trans	161.37°

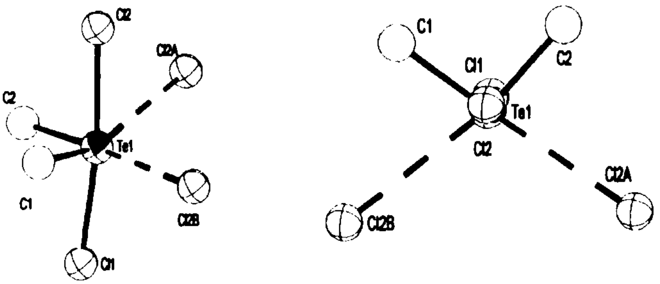


FIGURE 5. The coordination polyhedron in Me_2TeCl_2 [12]. Left: vertical view; right: view down the axial bonds.

Note that only Cl(2) of each molecule participates in secondary bonding, and as a result the Te-Cl(2) primary bond is slightly elongated in comparison with the Te-Cl(1) bond, as observed before for the ψ-octahedral geometry.

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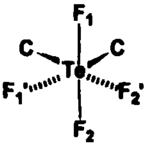
In the crystals of dimethyltellurium diiodide, α-Me_2TeI_2, [14] there are three independent molecules; all contain six-coordinate ψ-octahedral tellurium, but there are some differences in the bond angles and interatomic distances.

In diphenyltellurium(IV) difluoride, Ph_2TeF_2,[13] the coordination polyhedron displays a strong angular distortion, by the displacement of the secondary bonded fluorine atoms from the equatorial plane in opposite directions, as shown in FIGURE 6, and indicated by the values of the bond angles: F-Te···F 71.50° and 112.39°. The lone pair seems to be in the space of the wide F···Te···F angle of 115.74°.



(13)

$Te-F_1$	2.006 A	$Te-F_2$	2.006 A
$Te\cdots F_1'$	3.208 A	$Te\cdots F_2'$	3.208 A
Te-C	2.115 A		
F_1-Te-F_2	173.14°	C-Te-C	96.84°
C-Te-F (ax/eq)	87.6-87.8°		
$F_1-Te\cdots F_1'$	71.50°	$F_1-Te\cdots F_2'$	112.39°
$F_2-Te\cdots F_1'$	112.39°	$F_2-Te\cdots F_2'$	71.50°
$F_1'\cdots Te\cdots F_2'$	115.74°		
C-Te···F' cis	77.10°	C-Te···F' trans	158.31°

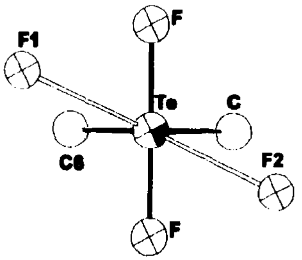


FIGURE 6. The coordination polyhedron in Ph_2TeF_2,[13]

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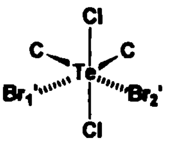
Bis(pentafluorophenyl)tellurium(IV) difluoride, $(C_6F_5)_2TeF_2$, is a dimer formed from two ψ-octahedra sharing an edge (connected through two Te-F···Te bridges).[34]

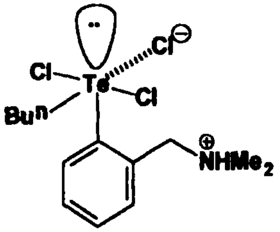
A different situation is observed in $(4\text{-}BrC_6H_4)_2TeCl_2$.(**14**) [35] In this compound the two additional secondary bonds, Te···Br (3.71 and 3.80 Å), are formed between tellurium and two *p*-bromine substituents of two neighbouring molecules; there are no Te···Cl secondary interactions, as demonstrated by the long interatomic distances (4.67 and 5.54 Å).



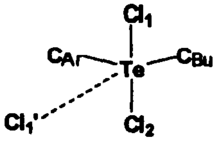
(14)

Te-Cl	**2.483 and 2.516 A**		
Te···Br1'	**3.71 A**	**Te···Br2'**	**3.80 A**
Te-C	**2.136 and 2.125 A**		
Cl-Te-Cl	**178.24°**	**C-Te-C**	**96.1°**
C-Te-Cl (ax/eq)	**89.2-90.0°**		

In [2-(butyldichlorotelluro)benzyl]dimethylammonium chloride (**15**)[36] the chloro anion forms a secondary bond with tellurium (3.337 Å) leading to a ψ-octahedral coordination geometry (with the lone pair in a vacant site) and an additional Te···Cl secondary bond.



(15)



Te-Cl_1	2.527 A	Te-Cl_2	2.487 A
Te···Cl_3	3.337 A	Te-Cl_1'	4.025 A
Te-C_{Ar}	2.134 A	Te-C_{Bu}	2.154 A
Cl_1-Te-Cl_2	171.9°	C-Te-C	97.8°
Cl-Te-C ax/eq	85.6-94.3°		
Cl_1-Te···Cl_3	97.48°	Cl_2-Te···Cl_3	90.27°
C_{Ar}-Te···Cl_3 trans	173.33°	C_{Bu}-Te···Cl_3 cis	76.67°
Cl_1-Te···Cl_1'	77.14°	Cl_2-Te···Cl_1'	106.88°
C_{Ar}-Te···Cl_1'	108.02°	C_{Bu}-Te···Cl_1'	147.21°
Cl_3···Te···Cl_1'	78.48°		

The Te···Cl(1)' distance is rather long, close to the sum of Van der Waals radii. This leads to two options for the coordination geometry, depending on whether this secondary bond is considered or not.

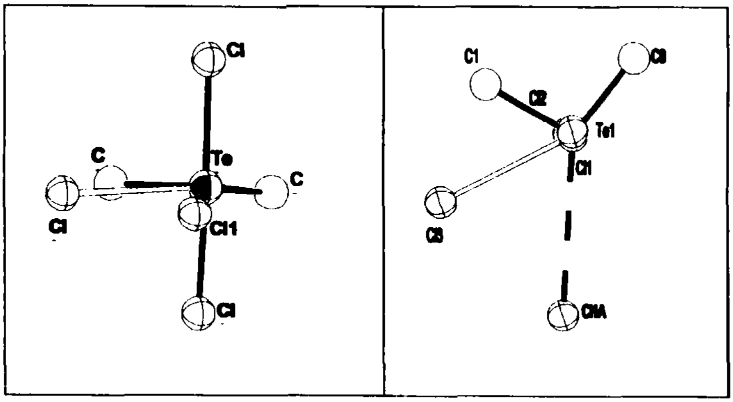


FIGURE 7. The coordination polyhedron in (15). Left: vertical view; right: view down the axial bonds.

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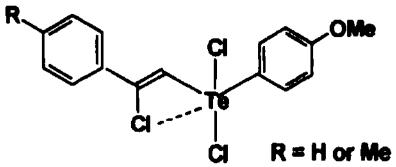
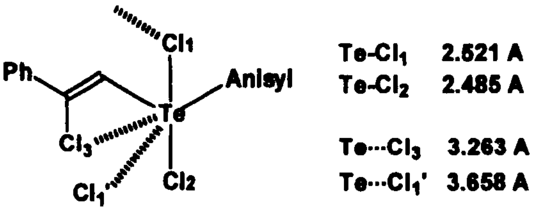
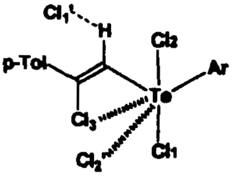
4.2. Intramolecular Te···halogen bonds

A particular case of this coordination geometry involves the structures in which one of the secondary bonds is intramolecular. This is possible if a donor site is present in the organic group in a position favourable for coordination to tellurium. Two illustrative examples are (2-chloro-2-phenylvinyl)(4-methoxyphenyl)tellurium(IV) dichloride, (PhClC=CH)(4-MeOC$_6$H$_4$)TeCl$_2$ (16) [37] and (2-chloro-2-*p*-tolylvinyl) (4-methoxyphenyl) tellurium(IV) dichloride, {*p*-Tol(Cl)C=CH}(4-MeOC$_6$H$_4$)TeCl$_2$(17).[38] In both compounds the 2-chloro substituent of the vinyl group forms an *intra*molecular Te···Cl secondary bond, in addition to a slightly longer *inter*molecular Te···Cl secondary bond in each molecular unit (FIGURE 8).





(16)



Te-Cl$_1$	2.478 Å	Te-Cl$_2$	2.521 Å
Te···Cl$_3$	3.280 Å	Te···Cl$_2$'	3.732 Å
Te-C$_{vinyl}$	2.085 Å	Te-C$_{aryl}$	2.117 Å
Cl$_1$-Te-Cl$_2$	177.65°	C-Te-C	94.1°
C-Te-Cl (ax/eq)	86.8-90.2°		
Cl$_1$-Te···Cl$_3$	79.65°	Cl$_1$-Te···Cl$_2$'	77.14°
Cl$_2$-Te···Cl$_3$	98.81°	Cl$_2$-Te···Cl$_2$'	101.91°

(17)

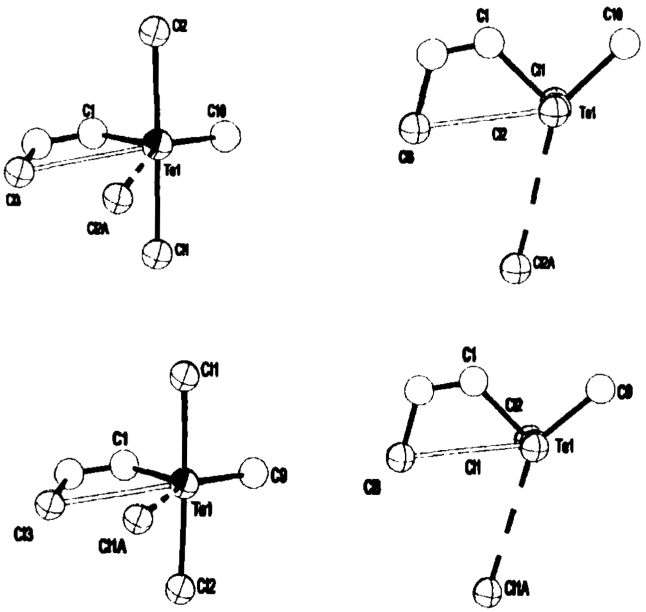


FIGURE 8. The coordination polyhedron in compound (16) (above) and (17) (below). Left: vertical view; right: view down the axial bonds.

The compounds were originally described as ψ-trigonal bipyramidal but a re-examination of the structures leads to the

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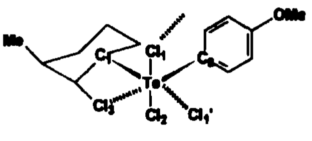
conclusion that their description as ψ-pentagonal bipyramidal reflects better the coordination geometry. This suggestion is supported by the bond angles.

The coordination polyhedra in the two compounds are very similar and FIGURE 8 illustrates it.

Peripheric halogen substituents on non-aromatic organic groups forming intramolecular secondary bonds to tellurium, and thus influencing the coordination geometry are illustrated by dichloro(p-methoxyphenyl)(*trans*-2-chloro-*trans*-3-methyl-1-cyclohexyl)tellurium (IV) (**18**).[39] The structure contains an intramolecular secondary bond Te⋯Cl(3) 3.268 Å and an intermolecular secondary bond Te⋯Cl(1') 3.927 Å (very weak, close to Van der Waals distance).



(18)

$Te-Cl_1$	2.487 Å	$Te-Cl_2$	2.586 Å
$Te\cdots Cl_3$	3.268 Å	$Te\cdots Cl_1'$	3.927 Å
$Te-C_1$	2.212 Å	$Te-C_8$	2.126 Å

$Cl_1-Te-Cl_2$	176.38°	C_1-Te-C_8	100.9°
C-Te-Cl ax/eq	86.8-96.7°		
$C_1-Te\cdots Cl_3$ cis	88.27°	$C_8-Te\cdots Cl_3$ trans	166.43°
$Cl_1-Te\cdots Cl_3$	94.32°	$Cl_2-Te\cdots Cl_3$	84.66°
$Cl_3\cdots Te\cdots Cl_1'$	60.15°		
$Cl_1-Te\cdots Cl_1'$	98.6°	$Cl_2-Te\cdots Cl_1'$	82.93°

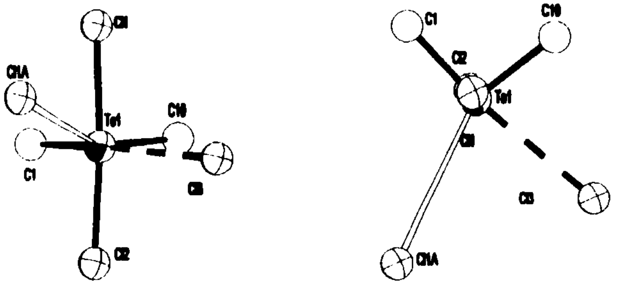


FIGURE 9. The coordination polyhedron in compound (**18**). Left: vertical view; right: view down the axial bonds.

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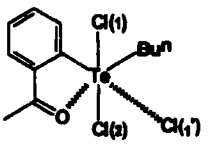
The coordination geometry is affected by angular distortions, as shown by the values of bond angles (recalculated from data deposited at Cambridge crystallographic Data Center). The coordination polyhedron is shown in FIGURE 9. It is a strongly distorted ψ-pentagonal bipyramid, with ample space for the lone pair in the C(1)-Te⋯Cl(1A) angle.

4.3. Intramolecular Te⋯oxygen bonds

Other examples of intramolecular secondary bonds leading to an increase of the coordination number and change of the geometry involve Te⋯O secondary bonds.

In 2-(butyldichlorotelluro)benzaldehyde,(19)[40] two independent molecules are connected into a dimeric structure through Te⋯Cl secondary bonds, each containing an intramolecular Te⋯O secondary bond.

The coordination polyhedron (redrawn from atomic coordinates deposited in the Cambridge Crystallographic Database) is illustrated in FIGURE 10.



Te-Cl$_1$	2.504 A	Cl$_1$-Te-Cl$_2$ 172.4°
Te-Cl$_2$	2.503 A	C-Te-Cl (ax/eq) 87.0-88.2°
Te⋯O	2.848 A	O-Te-C cis 68.8°
Te⋯Cl$_1$'	3.740 A	O-Te-C trans 166.8°
Te-C$_{Ar}$	2.121 A	C-Te-C 98.4°
Te-C$_{Bu}$	2.124 A	

(19)

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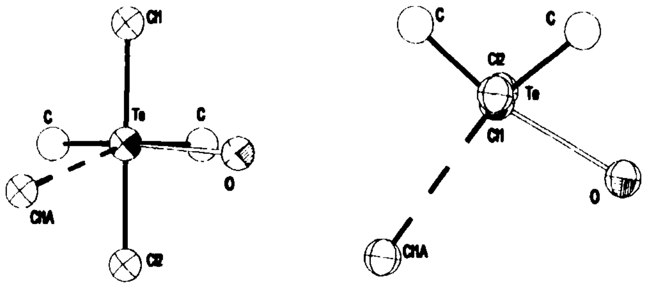

FIGURE 10. The coordination polyhedron in compound (**19**). Left: vertical view; right: view along the axial bonds.

The bond angles show that the Cl(1)' atom is displaced from the equatorial plane and this may suggest that a description of the coordination geometry as capped ψ-octahedron might be appropriate; the equatorial plane contains the two carbon atoms, the oxygen atom and has an apparently vacant site, presumably occupied by the lone pair. The Cl(1') atom which form the secondary bond is capping the lower face of the octahedron.

Another case of coordination geometry described as capped octahedron is found in dichloro(4-methoxyphenyl)(2-oxocyclohexyl) tellurium(IV) (**20**).[41] The crystal contains two independent molecules and the coordination polyhedra are shown in FIGURE 11.

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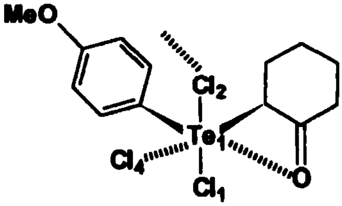
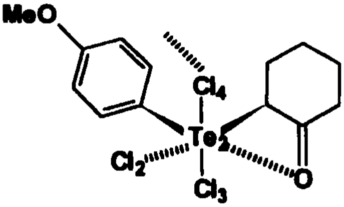


(20A)



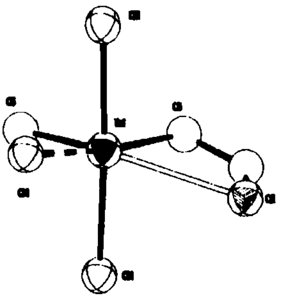
(20B)

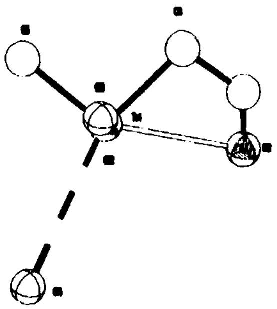
A

Te$_1$-Cl$_1$	2.542 A
Te$_1$-Cl$_2$	2.470 A
Te$_1$···Cl$_4$	3.679 A
Te$_1$···O	2.930 A
Cl$_1$-Te$_1$-Cl$_2$	174.4°
Cl-Te$_1$-C (ax-eq)	86.4-92.3°
C-Te-C	99.1°
Cl$_1$-Te$_1$···O	77.02°
Cl$_1$-Te$_1$···Cl$_4$	106.37°
Cl$_2$-Te$_1$···O	106.69°
Cl$_2$-Te$_1$···Cl$_4$	77.67°

B

Te $_2$-Cl$_3$	2.536 A
Te $_2$-Cl$_4$	2.400 A
Te $_2$...Cl$_2$	3.817 A
Te $_2$···O	2.94 A
Cl $_3$-Te$_2$-Cl$_4$	176.1°
Cl-Te $_2$-C (ax-eq)	86.7-91.0°
C-Te-C	99.10°
Cl$_3$-Te $_2$···O	83.09°
Cl$_3$-Te$_2$···Cl$_2$	111.36°
Cl $_4$-Te$_2$···O	96.30°
Cl$_4$-Te$_2$···Cl$_2$	72.41°





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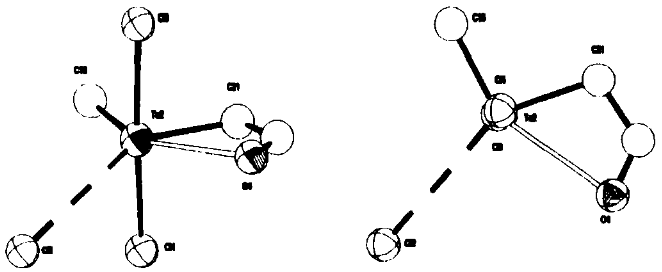
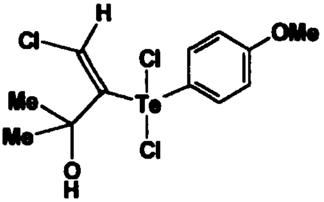
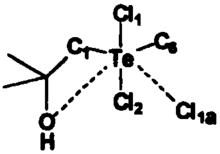


FIGURE 11. The coordination polyhedra in the two independent molecules of compound (**20**). Left: vertical view; right: view along the axial bonds.

In the first one [Te(1)] the oxygen atom forming the intramolecular secondary bond is displaced from the equatorial plane, towards Cl(1). In the second molecule [Te(2)] the secondary bonded chlorine atom presents a still more dramatic displacement from the equatorial plane, and the corresponding coordination geometry can be safely regarded as capped ψ-octahedral.

Dichloro[(E)-2-chloro-1-(2-hydroxyprop-2-yl)vinyl](4-methoxy phenyl)tellurium(IV) (**21**) also contains an intramolecular Te···O secondary bond (2.693 Å), an intermolecular Te···Cl secondary bond (3.485 Å) *trans* to the vinylic carbon, linking the molecule in a centrosymmetric dimer. Apparently a lone pair is in the equatorial plane and the chlorine atom secondary bonded to tellurium (which belongs to a symmetry related molecule) is capping a face of the octahedron.[42] Hydrogen bonds between the OH groups and Cl(2”) connect the dimers into tapes.

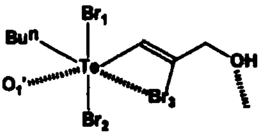




Te-Cl$_1$	2.4820 A	Te-Cl$_2$	2.560 A
Te···Cl$_{1a}$	3.4850 A	Te···O$_1$	2.693 A

Cl$_1$-Te-Cl$_2$	173.24°	C$_1$-Te-C$_6$	98.02°
C-Te-Cl (ax/eq)	87.06-92.86°		
Cl$_2$-Te···Cl$_{1a}$	106.21°		
C$_1$-Te···Cl$_{1a}$ trans	166.39°	C$_6$-Te...Cl$_{1a}$ cis	84.72°
Cl$_1$-Te···Cl$_{1a}$	78.5°		
Cl$_1$-Te···O$_1$	86.68°	Cl$_{1a}$···Te···O$_1$	120.35°
C$_1$-Te···O$_1$	56.10°	C$_6$-Te···O$_1$ trans	154.13°

Dibromo[(Z)-2-bromo-2-(hydroxymethyl)vinyl](*n*-butyl)tellurium (IV) (22)[43], with an intramolecular Te¨Br bond and an intermolecular Te...O bond displays a regulary-pentagonal bipyramidal geometry (polyhedron shown in FIGURE 12), with the lone pair in equatorial position.



(22)

Te-Br$_1$	2.7295 A	Br$_1$-Te-Br$_2$	176.59°
Te-Br$_2$	2.6115 A	C-Te-C	99.70°
Te···Br$_3$	3.488	Br-Te-C (ax/eq)	88.2-89.65°
Te···O$_1$'	3.041 A		
Te-C$_{vinyl}$	2.092 A	Te-C$_{Bu}$	2.134 A

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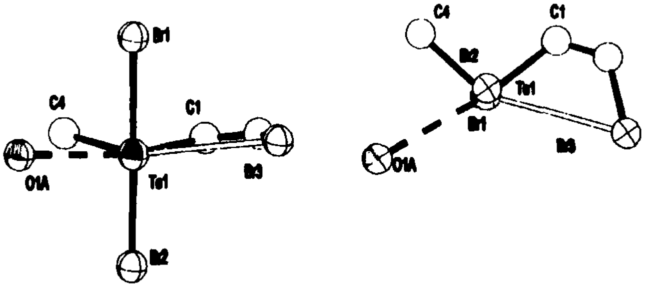

FIGURE 12. The coordination polyhedron in compound (22). Left: vertical view; right: view along the axial bonds.

This interpretation is supported by the bond angles: Br(3)···Te···O(1A) = 131.47°, Br(3)···Te···Br(1) = 80.21°, Br(3)···Te···Br(2) = 101.35°, Br(1)···Te···O(1A) = 82.83° and Br(2)···Te···O(1A) = 98.52°

In 1,1-dichloro-1-telluracyclohexane-3,5-dione $O(CO\text{-}CH_2)_2TeCl_2$ [44] there are two independent molecules, with two different coordinaton gemetries at tellurium. In one the tellurium atom forms only one intermolecular Te···O secondary bond (six-coordinate, ψ-octahedral), whereas in the other the tellurium atom forms two intermolecular Te···O secondary bonds (seven-coordinate, ψ-pentagonal bipyramial),. The molecules are associated to form double chains. The interatomic distances are: Te-Cl 2.493 and 2.512 Å in molecule A; 2.453 and 2.521 Å in molecule B; The Te···Cl distances are rather long (3.409 and 3.650 Å). The coordination polyhedra of the two telurium atoms are shown in FIGURE 13.

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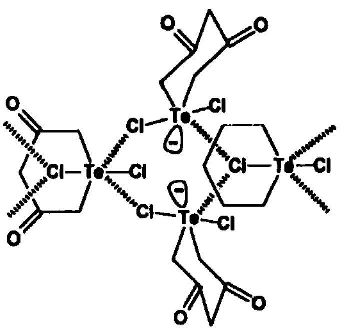


(23)

Te-Cl_1	2.493	2.453 A
Te-Cl_2	2.512	2.521 A
Te···Cl	3.409	3.650 A

C-Te-C	95.2°
Cl_1-Te-Cl_2	172.7°
C-Te-Cl (ax/eq)	86.4-88.7°

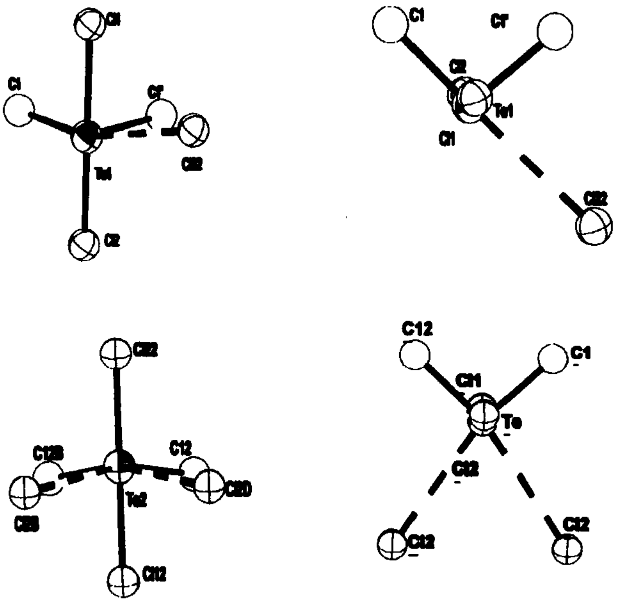
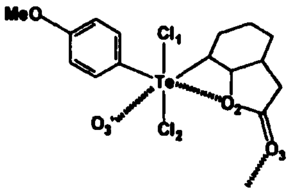


FIGURE 13. The coordination polyhedra in the two independent molecules of compound (23). Above: ψ-octahedron of Te(1); below: octahedron of Te(2), probably capped by the lone pair.

In dichloro(4-methoxyphenyl)(8-oxo-7-oxabicyclo[4.3.0]non-5-yl)tellurium(IV), (24), there are only tellurium-oxygen secondary bonds: one intramolecular [Te···O(2) 3.272 Å] and one intermolecular [Te···O(3') 3.292 Å]. The axial halogen atoms form only primary bonds (Te-Cl 2.545 and 2.499 Å) and are not involved in secondary bonds. The coordination polyhedron is a ψ-pentagonal bipyramid, with the lone pair presumably in the equatorial plane, as suggested by the measured bond angles (FIGURE 14).[45]



(24)

Cl_1-Te-Cl_2	176.7°	C-Te-C	100.6°
Cl-Te-C (ax/eq)	88.4-89.8°		
Cl_1-Te...O_3'	82.5°	Cl_1-Te...O_2	102.6°
Cl_2-Te...O_3'	100.8°	Cl_2-Te...O_2	76.31°
O_3'...Te...O_2	119.5°		
O_3'...Te-C_{Ar}	cis 95.1°		
O_3'..Te-C_{Cy}	trans 161.8°		
O_2...Te-C_{Ar}	trans 144.2°		

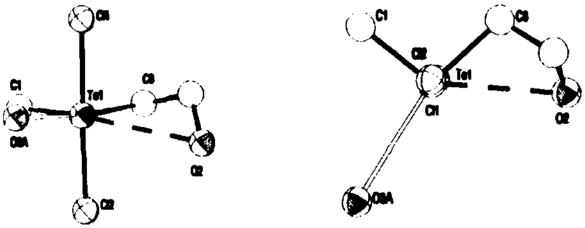


FIGURE 14. The coordination polyhedron in compound (24). Left: vertical view; right: view along the axial bonds.

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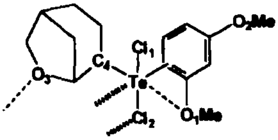
2',4'-Dimethoxyphenyl(trans-6-oxabicyco[3.2.1]oct-4-yl) tellurium(IV) (25) [46] also contains only Te···O intra- and intermolecular secondary bonds. The coordination polyhedron is shown in FIGURE 15.



(25)

Te-Cl_1	2.492 A	Te-Cl_2	2.539 A
Te...Cl_2'	3.771 A		
Te...O_1	2.943 A	O_3'...H-C_4	3.342 A
Cl_1-Te-Cl_2	177.2°	C-Te-C	100.6°
C-Te-Cl (ax/eq)	84.4-90.1°		
O_2...Te-C_8	51.27°	O_2....Te...Cl_2'	102.61°
C_8-Te...Cl_2'	152.56°	Cl_2-Te...Cl_2'	100.44°
Cl_1-Te...Cl_2'	81.76°	C_4-Te...Cl_2	106.61°

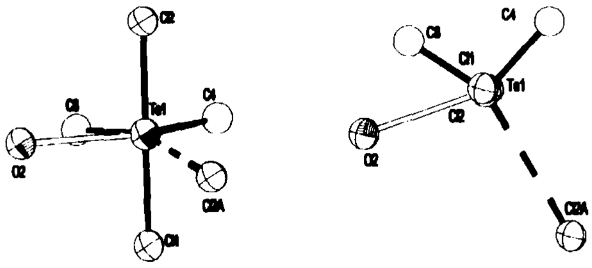


FIGURE 15. The coordination polyhedron in compound (25). Left: vertical view; right: view along the axial bonds.

4.4. Intramolecular Te···N bonds

In dichloro(4-ethoxyphenyl)[(2-benzylideneamino-5-methyl) phenyl]tellurium(IV) (26) the coordination geometry is deterimned by an intramolecular Te···N secondary bond (2.905 Å) and a weak

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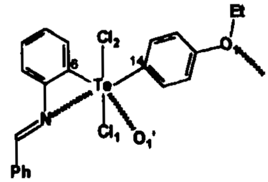
intermolecular Te···O(1') secondary interaction (3.605 Å).[47] The coordination polyhedron is shown in FIGURE 16. The lone pair is probably in the equatorial plane, in the wide angle O(1)'···Te···N (123.22°) of the distorted ψ-pentagonal bipyramid or capped ψ-octahedron.



(26)

$Te-Cl_1$	2.5373 A	Cl1-Te-Cl2	177.31°
$Te-Cl_2$	2.4968 A	C6-Te-C14	97.70°
$Te-C_6$	2.120 A	Cl1-Te···N	104.09°
$Te-C_{14}$	2.125 A	Cl2-Te···N	78.31°
$Te\cdots O_1'$	3.605 A	N···Te-C6 cis	53.60°
$Te\cdots N$	2.905 A	N···Te-C14 trans	147.19°
		N···Te···O1'	123.22°
		C6-Te···O1' trans	169.78°
		C14-Te···O1' cis	87.85°
		Cl2-Te···O1'	96.64°
		Cl1-Te···O1'	87.07°

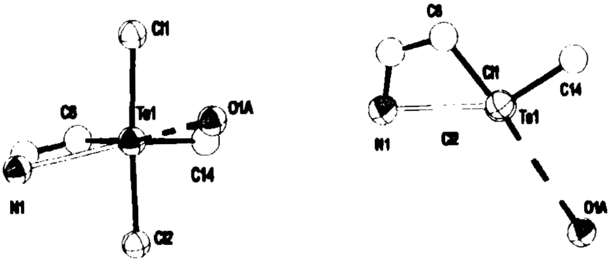
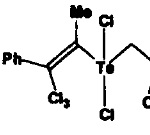


FIGURE 16. The coordination polyhedron in compound (26). Left: vertical view; right: view along the axial bonds.

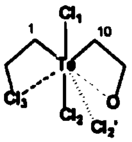
The values of the bond angles N···Te-C (cis) 53.6°, N···Te-Cl (axial-equatorial) 78.31° and 104.09° clearly indicate a displacement of the nitrogen atom out of the equatorial plane.

5. EIGHT-COORDINATE, COMPOUNDS OF $R_2TEX_2Y_3E$-TYPE COMPOUNDS

An unusually high cordination number is observed in acetonyl dichloro[(Z)-2-chloro-1-methyl-2-pneylethenyl]tellurium(IV), [{Ph(Cl) C=C(Me)}(MeCOCH$_2$)TeCl$_2$ (27).[48] In this compound, the tellurium atom forms three secondary bonds, in addition to the four primary bonds. Two secondary bonds are intramolecular [Te¨O 2.926 A and Te¨Cl(3) 3.180 Å] and a longer intermolecular Te¨Cl(2') secondary bond (3.659 Å) contributes to the connection of molecules into a spiral chain. The coordination polyhedron is shown in FIGURE 17. The geometry is that of a capped ψ-pentagonal bipyramid, with the lone pair in equatorial position (in the O¨Te-Cl(2) bond angle) and Cl(2)'in the capping position (coordination number 8) on the Cl(1)-C¨Cl(2') face.



(27)



Te-Cl$_1$	2.6096 A	Te-Cl$_2$	2.4870 A
Te-C$_1$	2.119 A	Te-C$_{10}$	2.122 A
Te...Cl$_3$	(intramolecular)	3.180 A	
Te...Cl$_2$'	(intermolecular)	3.659 A	
Cl$_1$-Te-Cl$_2$	171.78°		
C-Te-C	97.59°		
C-Te-Cl (ax/eq)	86.28-88.07°		

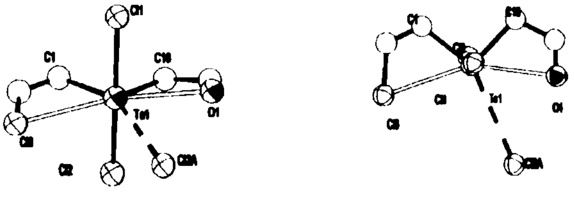


FIGURE17. The coordination polyhedron in compound (27). Left: vertical view; right: view along the axial bonds.

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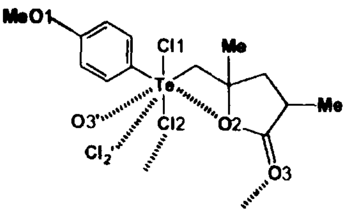
Dimethyl-5-oxo-2,3,4,5-tetrahydro-2-furyl)methyl]-(4-methoxy phenyl)-tellurium(IV) (28)[49], contains an intramolecular Te···O secondary bond (3.006 Å) in addition to the intermolecular Te···Cl secondary bond (3.824 Å) and the geometry initially reported as ψ-trigonal bipyramidal should be described as capped ψ-pentagonal bipyramidal. The lone pair is probably located in the O···Te···Cl(2') angle or below it. The coordination polyhedron is shown in FIGURE (18).



(28)

Te-Cl_1	2.517 A	Te-Cl_2	2.495 A
Te···O_2	3.006 A	Te···O_3	??
Te···Cl_2'	3.824 A		
Cl_1-Te-Cl_2	173.45°	C-Te-C	96.5°
C-Te-Cl ax/eq		86.06-88.72°	

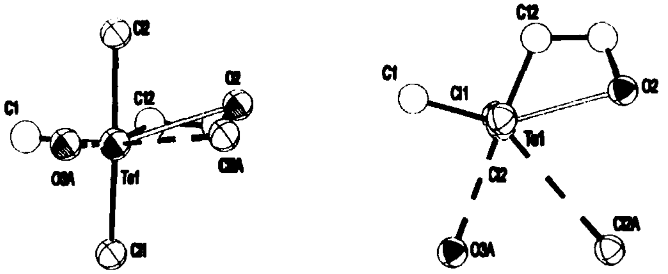


FIGURE 18. The coordination polyhedron in compound (28). Left: vertical view; right: view along the axial bonds.

Dibromo-bis(2-bromovinyl)tellurium(IV)(29)[50] forms a capped

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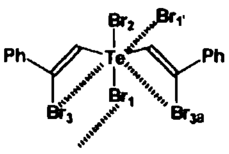
ψ-pentagonal bipyramidal polyhedron, with the Br(1A) atom displaced from the equatorial position and capping the Br(2)-Br(3)-Br(3A) face, apparently to leave room for the lone pair. The polyhedron is illustrated in FIGURE 19. This is supported by the bond angles observed.



(29)

Te-Br$_1$	2.624 A	Te-Br$_2$	2.732 A
Te···Br$_3$	3.252 A	Te···Br$_{3a}$	3.252 A
Te···Br$_1$'	4.329 A		
Br$_1$-Te-Br$_2$	171.07°	C-Te-C	99.20°
Br-Te-C (ax/eq)	85.25-88.97°		
C-Te···Br$_3$ cis	57.42°	C-Te···Br trans	156.46°
Br$_2$-Te···Br$_3$	94.59°	Br$_2$-Te···Br$_1$'	78.86°
Br$_1$-Te···Br$_3$	88.00°	Br$_1$-Te···Br$_1$'	110.07°
Br$_3$···Te···Br$_1$'	74.74°	Br$_3$···Te···Br$_3$'	145.68°

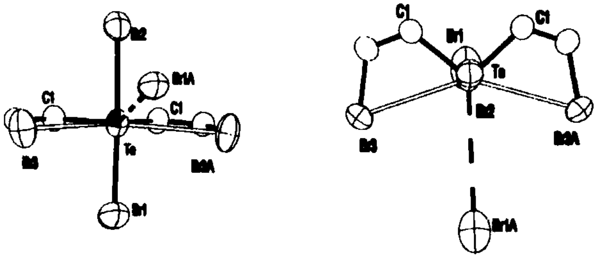


FIGURE 19. The coordination polyhedron (capped ψ-pentagonal bipyramid) in compound (29). Left: vertical view; right: view along the axial bonds.

7. OTHER TYPES

A unique coordination geometry was identified in the compound

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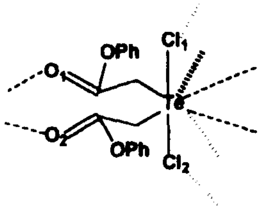
{PhOC(O)CH$_2$}$_2$TeCl$_2$ **(30)**[51] The X-ray crystal structure of the compound has been described as ψ-trigonal bipyramidal, like the other diorganotellurium(IV) derivatives, but the re-examination based upon the data deposited at Cambridge Crystallographic Data Centre reveals additional intermolecular interactions at shorter than Van der Waals distances: two intermolecular secondary Te···Cl bonds, two intermolecular secondary Te···O bonds, leading to a coordination geometry in which each tellurium atom forms four covalent and four secondary bonds. The resulting coordination polyhedron is a distorted square antiprism, in which one of the faces seems to accommodate a protruding lone pair (FIGURE 20. The polyhedron displays, severe radial and angular distortions (off-center tellurium atom) caused by the significantly differing primary and secondary bond lengths. The four intermolecular interactions lead to a supramolecular stucture based upon Te-Cl double chains interconnected through pairs of Te···O secondary bonds.



Te-Cl$_1$	2.516 A
Te-Cl$_2$	2.507 A
Te...Cl$_1$'	3.726 A
Te...Cl$_2$'	3.699 A
Te...O$_1$'	3.365 A
Te...O$_2$'	3.422 A

Cl$_1$-Te-Cl$_2$	172.9°
C-Te-C	97.3°
C-Te-Cl (ax/eq)	86.9-89.7°
Cl$_1$-Te...Cl$_1$'	112.02°
Cl$_1$-Te...Cl$_2$'	71.33°
Cl$_1$-Te...O$_1$'	70.41°
Cl$_1$-Te...O$_2$'	117.73°
Cl$_1$'...Te...Cl$_2$'	126.88°

(30)

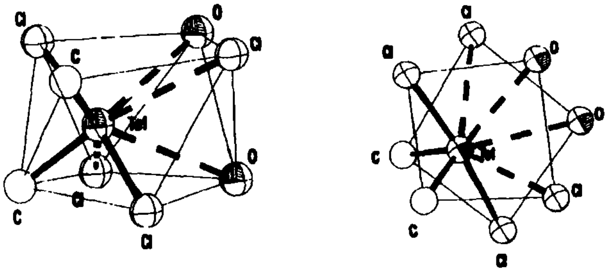
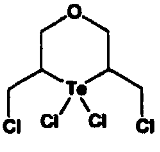
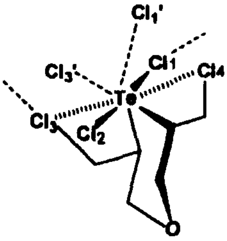


FIGURE 20. The coordination polyhedron (distorted square antiprism)in compound (30). No space is assigned to the lone pair.

Another compound in which tellurium has an unusual high coordination number is dichloro-*cis*-3,5-di(chloromethyl)-1,4-oxa tellurane(IV) (31). The tellurium atom forms four secondary [two intramolecular, Te Cl(3) and Te Cl(4) and two long intermolecular Te Cl(1') and Te Cl(3") 4] bonds in addition to the four primary bonds [Te-C, Te-Cl(1)and Te-Cl(2)].[52] With the lone pair the coordination number would be raised to nine but no space is assigned to it. The coordination polyhedron is a capped petagonal bipyramid (FIGURE 21).



(31)



Cl_1-Te-Cl_2	176.9°
C-Te-C	94.0°
C-Te-Cl (ax/eq)	88.6-89.7°
Te-Cl_1	2.606 A
Te-C	2.163; 2.166 A
Te-Cl_2	2.487 A
Te···Cl_3	3.416 A
Te···Cl_4	3.467 A
Te···Cl_1'	3.808 A
Te···Cl_3'	4.014 A

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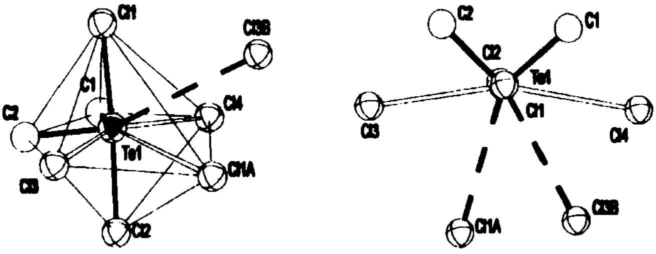

FIGURE 21. The coordination polyhedron (capped pentagonal bipyramid) in compound (31). No space is assigned to the lone pair.

6. TELLURIUM π...C_6H_5 INTERACTIONS

An unusual situation occurs in (Z)-1-(dichloro-p-methoxyphenyl telluro)-1-phenyl-2-thiophenylethene (32).[53] A re-examination of structure data showed that there are no secondary interactions between tellurium and any other potential donors within a distance of 4.5 Å, but the compound is a dimer and a rather short distance of 3.4 Å between the tellurium atom and the centroid of a phenyl ring from a symmetry related molecule is observed, indicating a novel Te π···C_6H_5 interaction, not reported before.[54] The lone pair is pointing somewhere towards this phenyl ring, which is unprecedented and unexpected. If the vicinity of the phenyl is ignored the tellurium atom is five-coordinate, with a site occupied by the lone pair. The coordination polyhedron is shown in FIGURE 22.

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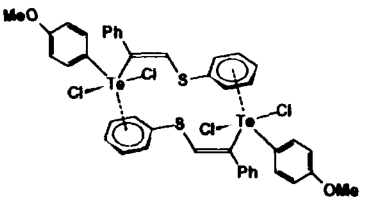


Te-Cl	2.514 and 2.501 A
Te-C	2.121 and 2.127 A
Cl-Te-Cl	173.07°
C-Te-C	99.92°
C-Te-Cl (ax/eq)	85.36-90.09°

(32)

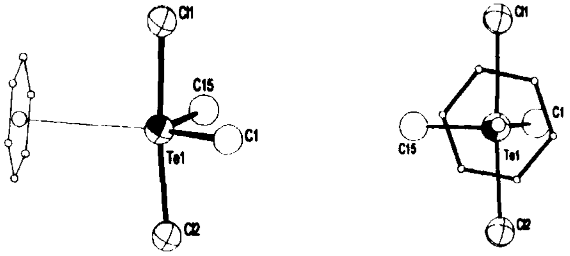
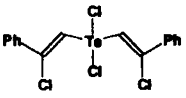


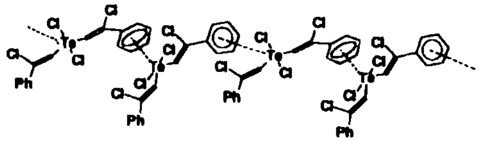
FIGURE 22. The coordination polyhedron of compound (32).

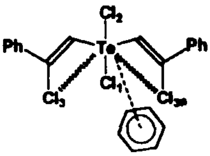
If the phenyl is, however, considered as a ligand, the central tellurium atom should be regarded as six-coordinate and the geometry should be described as ψ-octahedral.

A puzzling structure is that of dichloro-bis(2-chlorovinyl) tellurium(IV) (33).[55] The compound is associated through weak Te···π-C_6H_5 interactions. The coordination polyhedron is a pentagonal bipyramid with one equatorial position occupied by the phenyl ring of an adjacent molecule (FIGURE 23).



(33)





(33)

Te-Cl_1	2.5062 A	Te-Cl_2	2.5186 A
Te···Cl_3	3.2901 A	Te···Cl_{3a}	3.2542 A
Te···Ph centroid	3.7576 A		
Te-C_1	2.0960 A	Te-C_2	2.0869 A
Cl_1-Te-Cl_2	175.23°	C-Te-C	93.19°
Cl-Te-C (ax/eq)	87.1-91.38°		
Cl_2-Te···Cl_3	99.44°	Cl_2-Te···Cl_{3a}	83.09°
Cl_1-Te···Cl_3	83.15°	Cl_1-Te···Cl_{3a}	95.67°
Cl_3···Te···Cl_{3a}	162.18°		
Cl_3···Te···centroid	79.13°	Cl_3'···Te···centroid	83.36°
Cl_1-Te···centroid	96.63°	Cl_2-Te···centroid	87.82°
C_1-Te···centroid	129.40°	C_2-Te···centroid	136.84°

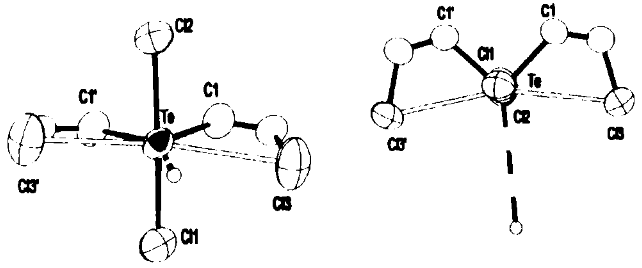


FIGURE 23. The coordination polyhedron in compound (33). Left: vertical view; right: view down the axial bonds.

The tellurium atom forms four primary bonds (Te-C and Te-Cl), two intramolecular secondary Te···Cl bonds and faces a phenyl group of a symmetry related molecule. The distance between tellurium and the ring centroid is 3.7576 Å, shorter than the sum of Van der Waals radii

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of tellurium and carbon. We tentatively suggest that the lone pair is located between the π-bonded phenyl ring and the central tellurium atom, in the wide Cl(3)···Te···Cl(3a) angle (162.18°).

It is quite possible that similar weak π-interactions between tellurium atoms and aromatic groups are present in other organotellurium compounds and passed unnoticed so far.

9. CONCLUSIONS AND OUTLOOK

The coordination geometry of the central atom in diorganotellurium(IV) halides, is in fact much more diversified than in almost invariable literature descriptions as ψ-trigonal bipyramidal. Thus, ψ-trigonal bipyramidal, ψ-octahedral, ψ-pentagonal bipyramidal and some others coordination geometries dictated by higher coordination numbers, are achieved through aditional intra- and intermolecular secondary bonds. Therefore, a careful examination of organotellurium structures is necessary when X-ray diffraction analyses are performed, in order to identify correctly the coordination polyhedra which may result from supramolecular self-assembly of the monomeric molecules or from intramolecular secondary bonds.

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