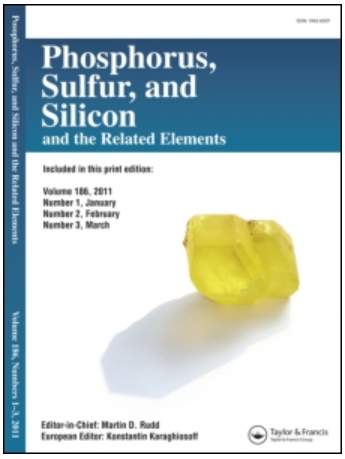

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RECENT DEVELOPMENTS IN THE STRUCTURAL CHEMISTRY OF TELLURIUM WITH SULFUR AND SELENIUM CONTAINING LIGANDS

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Since the author's last surveys of this field in 1983 and 1987,[1,2] there has been considerable developments in the structural chemistry of tellurium. A comprehensive review covers the field through most of 1993.[3]

Much of the recent activity concerns structures of Te(IV) compounds. The majority of these can be derived from R_nTeX_{y-n} (n = 0-3; y = 4; R = Me, Ph, MeOPh; X = halogen) by replacing halogens successively with bidentate dithiolate ligands such as alkylxanthates, dialkyldithiocarbamates, dialkyldithiophosphates and dialkyldithiophosphinates. These highly coordinated compounds mostly have coordination numbers 6 and 7, counting the lone electron pair and secondary bonds. The coordination spheres around the central tellurium atom consequently are based on octahedral and pentagonal bipyramidal geometries.

For Te(II), structures of interesting new planar three and four-coordinate compounds have appeared with both monodentate and bidentate thio and seleno ligands. T-shaped, square planar and trapezoid planar coordination geometries dominate.

Keywords: Tellurium complexes, S + Se ligands.

I. INTRODUCTION

Although tellurium commonly displays oxidation states from -2 to +6 (in steps of 2), compounds with sulfur containing ligands usually have oxidation numbers +2 and +4. The maximum oxidation number 6, seems to require highly electronegative ligands like F^- and ligands with oxygen as donor atom.

For Te(II) complexes, linear L_1-Te-L_2 systems predominate. Most Te(II) complexes have T-shaped or square planar or distorted square planar geometries. A T-shaped complex is believed to be composed of a 3c - 4e system at right angles to a 2c - 2e system, while a square planar complex is composed of two interprenetrating 3c - 4e systems at right angles to each other. In such linear systems, the L-Te distance is usually much longer than the sum of the covalent radii of the tellurium and ligand atoms. This has been explained by 3c - 4e bonding in such systems. As long as such a three - center system is relatively symmetric with respect to bond lengths and angles, the Te(II) radius seems to be fairly constant and close to 1.64 Å. For Te(IV) compounds, 3c - 4e bonding is known from octahedral complexes where there are three 3c - 4e systems at right angles to each other. In other symmetries the picture is more complicated. [1,3]

The differing *trans* influences of ligands situated *trans* to each other are a common source of assymmetry. Greatly assymmetric 3c - 4e systems are quite common, and in such cases the stronger bond approaches a covalent 2c - 2e bond while the other bond approaches a van der Waals contact. Such weak bonding is commonly termed secondary[4] or hypervalent, and is very common among tellurium compounds with chalcogen containing ligands and halide ligands.

Organization

In this review Te(II) complexes will be discussed first and then Te(IV) complexes. Compounds with monodentate chalcogeno ligands will be discussed before those with bidentate dichalcogeno ligands. Two-coordinate Te compounds and polytellurides are not included. Compounds described in the earlier reviews[1-3] will only rarely be discussed.

Figures

Only the coordination spheres of Te are shown. Bond lengths shown are in Å; Te-C bonds are mostly in the range 2.12 (0.04) Å and are not given. For **1** and **9**, bond lengths are averages from two indepedent molecules. Dashed atoms are related to the original ones

by a center of symmetry. For **34,** Te-I and not Te-Br bond lengths are given.

Abbreviations.

S-O	bidentate mixed oxygen and sulfur containing ligand
S-S	bidentate sulfur containing ligand
Se-Se	bidentate selenium containing ligand
mbts	N-methylbenzothiazole-2(3H)-selone
bipy	4,4-bipyridine
Me	methyl
Et	ethyl
i-Pr	isopropyl
Ph	phenyl
phen	1,10-phenanthroline^{+}

II. TE(II) COMPLEXES WITH MONODENTATE SULFUR OR SELENIUM LIGANDS

1. Three-coordinate T-shaped complexes with RTeSX and RTeSeX coordination

There are only three new compounds among these, all with R = Ph and X = Br.[5,6] The chalcogen ligands are all situated *trans* to halogen which is normal for such compounds. The three compounds are bromo[N-methylbenzothiazole-2(3H)-selone]phenyltellurium(II), **1**,[5] bromophenyl[tris(dimethylamino)phosphane-selenide]tellurium(II), **2**,[5] and bromophenyl- [1-phenyl-3-(1′, 3′-thiazol-3′-ium-2′-yl)-isothioureidato]tellurium(II), **3**.[6] They all have the expected T-shape with C(phenyl) at the stem and the 3c - 4e X-Te-S(e) sequence at nearly right angles to this. In such systems, there is often a weak intermolecular contact *trans* to the Te - C bond. At first glance, none of these compounds have such a contact. However, a closer inspection reveals a weak interaction between Te and the π system of the -S-C(=Se)-NMe group of the Se ligand in the molecules of **1**, where the distances from Te to the C atom of a Se ligand in a neighbor molecule are only 3.655(1) and 3.911(1) Å. This is shown in

Figure 1a. Such π interactions involving Te was first found for a Te(IV) complex,[7] and may have been overlooked in earlier structural work.[5,8] There are no intermolecular interactions involving Te in **2** and **3**.[5,6]

2. Four-coordinate square planar complexes with TeE_nX_{4-n} (n = 1-4, E = S, Se) coordination

Since the last review,[3] there seems to be no new compounds in this group, where thio- and selenoureas used to be the most common chalcogeno ligands. However, one may mention the tellurium dimethylselenourea complex cation, $\{Te[Me_2NC(=Se)NH_2]_4\}^{2+}$, **4**.[9] Here we have a Te(II) complex with a $TeSe_4$ coordination sphere. Also the complex bromotris(1-methylimidazole-2-(3H)-thione)-tellurium(II), **5**, is worth mentioning here as it has the seldom found TeS_3X coordination sphere.[10]

III. TE(II) COMPLEXES WITH BIDENTATE DICHALCOGENO LIGANDS

1. Three-coordinate T-shaped complexes with $RTeS_2$ coordination

Structures of such complexes are of a relatively recent date. R = Ph or MeOPh and the ligands are $R_2PS_2^-$, $(RO)_2PS_2^-$ and $ROCS_2^-$. The first of these structures were published by Husebye *et al* around 1990.[11,12] Here one of the ligand sulfur atoms forms a nearly covalent bond to Te. Also the Te-C bond is a normal covalent bond. The second sulfur atom of the bidentate ligand forms a weak, secondary bond to the Te atom of a neighbor molecule, thus completing the T shape. The next compound in this series, $PhTe(Ph_2PS_2)$, **6**, [13,14] obtains its three-coordination in a different manner. Here it is the sulfur atom strongly bonded to tellurium that forms the weak intermolecular Te---S bond to tellurium in a neighbour molecule. The other sulfur atom does not participate in such bonds at all. The last of the T-shaped compounds is rather unusual. The dimeric 4-methoxyphenyltelluriumtetraphenyl-dithioimidodiphosphinate, $\{MeOPhTe[N(Ph_2PS)_2]\}_2$, **7**, [15] has an asymmetric S-Te-S 3c - 4e system with Te-S = 2.551(3) and

2.873(3) Å. At right angles to the S-Te-S sequence there is a Te-C(Ph) bond of 2.10(1) Å. Roughly *trans* to the Te-C bond, there is a long Te---Te contact across the twelve-membered ring of 3.761(1) Å.The structure is shown in Figure 1b and is nearly the same as that found for the corresponding phenyl compound.[16]

2. Four-coordinate, square planar and trapezoid planar complexes with TeE_4 (E = S, Se) coordination

Heteropolychalcogenides may form square planar TeS_4 and $TeSe_4$ coordination. The former is found in the anion $Te(S_5)_2^{2-}$, **8** [17] (Figure 1c), where the pentasulfide anions function as bidentate ligands. The two six-membered rings fused at Te have chair forms. As a curiosity it can mentioned that the $Te(Te_3)_2^{2-}$ anion has a square planar $TeTe_4$ coordination. [18]. The structure of the complex $Te[N(Ph_2PSe)_2]_2$, **9**, has just been solved. [15] Here we have a square planar $TeSe_4$ coordination involving six-membered rings with chair forms as in **8** (Figure 1d). Also **9** is isomorphous with its sulfur analogue. [19] The Te-Se bond lengths are in the range 2.775(1) to 2.815(1) Å, normal for 3c - 4e bonding. [1,3]

Before mentioning new trapezoid planar complexes, the complex anion $\{Te[(NC)_2C{=}CSe_2]_2\}^{2-}$, **10**, should be mentioned. [20] The structure is centrosymmetric with a square planar $TeSe_4$ group with an average Te-Se bond length of 2.683 Å. This is much shorter than the corresponding distances in **9**, and far too short for a 3c - 4e system. In such a system, Te has a radius near 1.64 Å.[1] Adding this to the covalent radius of Se, 1.17 Å, [21] gives an expected Te-Se bond length of 2.81 Å. However, the temperature parameters of Te and Se atoms are very high. This may indicate disorder, for instance a statistical distribution of trapezoid planar molecules where half of the molecules are turned 180 degrees.

There are only two truly trapezoidal planar molecules in this group. The structure of $(AsPh_4)_2\{Te[(NC)_2C{=}CS_2]_2\}$, **11**, is mentioned here because of the theoretical calculations done. [22] They show that the trapezoid form allows a mixing of *s* and *p* orbitals on Te and lessens repulsions between its two lone pairs of electrons. Contributions of *s* orbitals in this manner was indicated earlier by measuring the Mössbauer effect of similar Te(II) compounds. [23] The complex anion with the mixed S, Se ligand, $\{Te[(NC)_2C{=}CSSe]_2\}^{2-}$,

12, [20] has the expected trapezoid planar structure with strong Te-Se bonds (ave 2.614 Å) and weak Te-S bonds (ave 2.846 Å), see also Figure 1e.

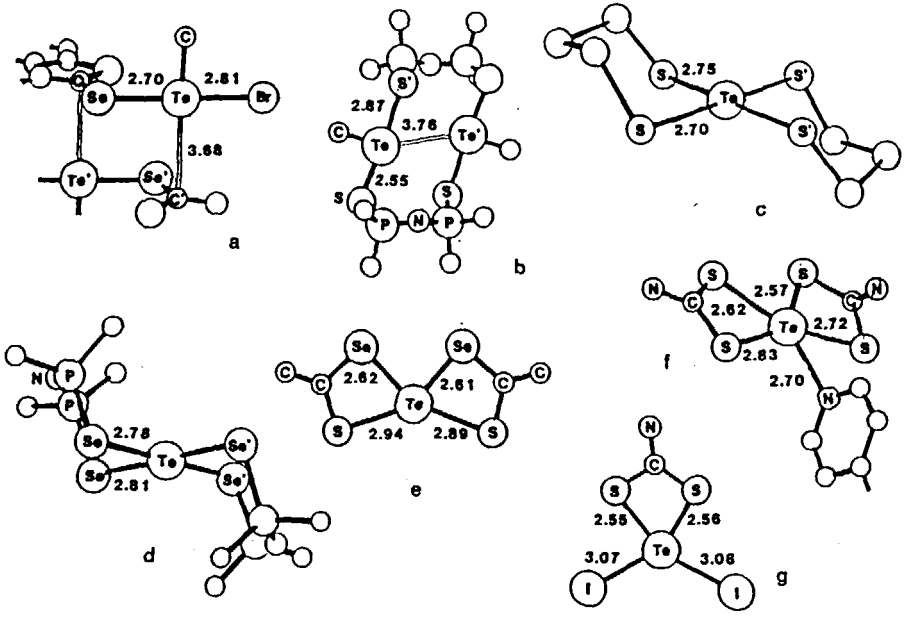

FIGURE 1. Selected structures of Te(II) compounds.
a, PhTeBr(mbts), **1**; b, $\{PhTe[N(Ph_2PS)_2]\}_2$, **7**; c, $Te(S_5)_2^-$, **8**; d, $Te[N(Ph_2PSe)_2]_2$, **9**; e, $Te[(NC)_2C{=}CSSe]_2^{2-}$, **12**; f, $Te(Et_2NCS_2)I_2$, **15**; g, $[Te(Et_2NCS_2)_2]_2 \cdot bipy$, **19**.

3. Four-coordinate , trapezoid planar complexes with TeS_2X_2 coordination

There are six compounds in this group. The first three represent a new type of complex containing the anion $TeX_2(Et_2NCS_2)^-$. The compounds $H(phen)_2[TeBr_2(Et_2NCS_2)]$, **13**,[24] $H(phen)_2[TeI_2(Et_2NCS_2)]$, **14**[24] and $(Et_4N)[TeI_2(Et_2NCS_2)]$, **15**,[24] all have similar structures of their complex anions. The bidentate ligands are nearly isobidentate and the Te-S bond lengths are in the range 2.503(2) to 2.567(2) Å. The Te-X distances show more variation as Te-Br bond lengths are 2.911(1) and 2.986(1) Å while the Te-I bond lengths range from 3.038(1) - 3.151(1) Å. The structure of **15** is shown in Figure 1f. However, also for these compounds a normal tellurium radius near 1.64 Å is found, corresponding to 3c - 4e bonding. These compounds have the same type of structure as the next three compounds, $TeCl(Et_2NCS)$, **16**,[25] $TeBr(Et_2NCS_2)$, **17**,[25] and $TeI((Et_2NCS_2)$, **18**,[26]. These latter compounds obtain their four-coordination by forming polymeric spirals through intermolecular Te---X secondary bonds. These are of course weaker than the *cis* situated Te-X bonds and this asymmetry leads to corresponding asymmetries in the *trans* situated Te-S bonds, leading to slightly anisobidentate dithiocarbamate ligands. By replacing half of the terminal halogens with bridging ones, as compared to **13**, **14** and **15**, the last three compounds form on the average longer Te-X bonds and shorter Te-S bonds.

4. Five-coordinate planar complexes with TeS_4N coordination

The only complex of this rare type is the adduct resulting when two molecules of $Te(Et_2NCS_2)_2$ are held together by weak Te---N bonds of 2.700(2) Å from a bridging 4,4-bipyridyl molecule, $[Te(Et_2NCS_2)_2]_2bipy$, **19**.[27] The asymmetry in the Te-S bonds is smaller than usually found in free TeL_2 (L = dithiocarbamates), but the average Te-S bond length of 2.686 Å is normal.[1] Weak intermolecular Te---S contacts are also common in Te(II) bis(dialkyldithiocarbamates and bis(alkylxanthates).[1]

IV. TE(IV) COMPLEXES WITH MONODENTATE LIGANDS

There is only one new complex in this category, namely $Ph_3Te(4\text{-}ClPhS)$, **20** [28]. The phenylthiolate ligands act as bridges via the sulfur atom. The result is a centrosymmetric, cyclic eight-membered ring tetramer where all Te atoms have a TeC_3S_2 coordination sphere with the carbon atoms facial. Including the stereochemically active LP on Te results in a ψ-octahedral structure for this complex. One of the Te atoms with it's coordination sphere is shown in Figure 2a.

V. TE(IV) COMPLEXES WITH BIDENTATE SULFUR CONTAINING LIGANDS

The great majority of these compounds have aryl or alkyl ligands in addition to sulfur containing ligands. Most of them also have halogen ligands. The compounds in this category who recently have had their structures determined are all six - or seven-coordinate. Several have been discussed in a recent overview.[29]

1. Complexes Te(S-S)X_4

In this category there is only one complex, $TeCl_4[CH_2(Ph_2PS)_2]$, **21.**[30] The neutral, large-bite dithio ligand occupies two positions in an octahedral coordination sphere around tellurium, as shown in figure 2b. Surprisingly, the Te-Cl bonds *trans* to the Te-S bonds are shorter than the two Te-Cl bonds who are *trans* to each other, with average Te-Cl bond lengths of 2.374 and 2.502 Å, respectively. Correspondingly, the Te-S bonds are long and weak [Te-S1 = 2.891(3) and Te-S2 = 2.633(4) Å], indicating a larger *trans* influence for halogen compared to sulfur containing ligands contrary to what is expected. However, also here there are large thermal parameters for the ligands which may indicate disorder.

2. Complexes of the type Te(S-S)$_n X_{4-n}$ where n = 1 and 2

Only two such structures are new. The ψ-octahedral complex $Te(Et_2NCS_2)I_3$, **22,**[31] seems to be the first of its kind with n = 1. (Figure 2c). The molecules are linked together by weak intermolecular Te---I contacts of 3.516(1) and 3.677(1) Å to two

different neighbors. Inclusion of these contacts results in a greatly distorted pentagonal bipyramidal structure where both sulfur atoms plus three iodines (two of which are bridging and belong to two neighbor molecules) are equatorial and the remaining two iodines are axial.

The complex $Te(Et_2NCS_2)_2I_2$, **23**,[32] has n = 2 and is shown in Figure 2d. Pairs of complexes are knit together by secondary, intermolecular Te---I bonds of 3.380(2) Å. This originally axial I atom takes up the fifth equatorial position in a pentagonal bipyramidal configuration in a neighbor molecule. This bridging iodine has a longer Te-I bond than the nonbridging one: 3.048 (2)

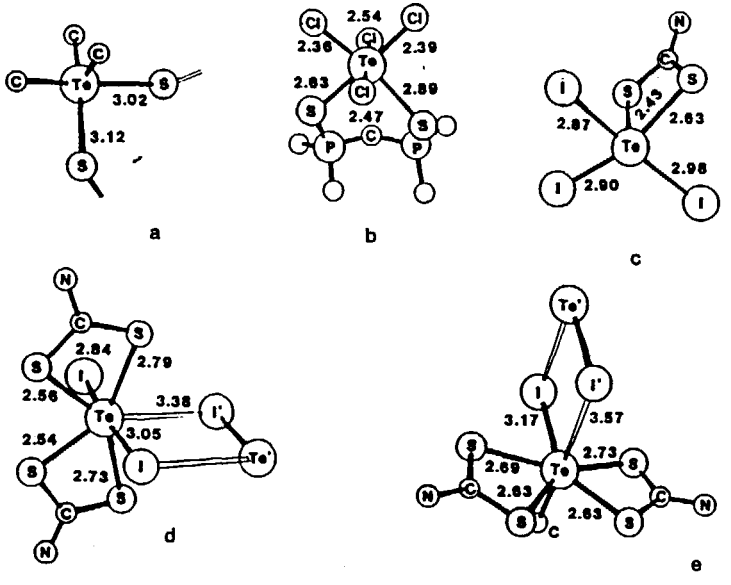

FIGURE 2. Structures of some Te(IV) compounds. a, one of the two independent Te coordination spheres in $Ph_3Te(4\text{-}ClPhS)$, **20**; b, $TeCl_4[CH_2(Ph_2PS)_2]$, **21**; c, $Te(Et_2NCS_2)I_3$, **22**; d, $Te(Et_2NCS_2)_2I_2$, **23**; e, $4\text{-}MeOPhTe(Et_2NCS_2)_2I$, **31**.

compared to 2.835 (2) Å. These bonds are both axial and their lengths may be compared to an expected 3c - 4e bond length of 2.97 Å.

3. Complexes of the type RTe(S-S)$_3$.

There are only three new structures in this group, and they are all quite similar: The first, PhTe[PhO)$_2$PS$_2$]$_3$, **24**,[33] is quite interesting since earlier attempts by the author to make such complexes with dialkyldithiophosphates failed. It has the very distorted pentagonal bipyramidal structure known from the corresponding diethyldithiocarbamate,[34,35] the first such complex made. However, the average Te-S equatorial bond length of 2.830 Å is much longer than the average found in two recent dialkyldithiocarbamate derivatives, PhTe(Et$_2$NCS$_2$)$_3$ (triclinic version)[35], **25**, and 4-MeOPhTe-(Et$_2$NCS$_2$)$_3$, **26**.[35] There the Te-S$_{eq}$ bond has an average bond length value of 2.715 Å, reflecting the stronger nucleophilicity of dithiocarbamates as compared to dithiophosphates (see also ref. 29). The weak axial Te-S bond (*trans* to Te-C) varies in the same manner (3.374 and 3.224 Å). This weaker nucleophilicity of dithiophosphosphate ligands has been documented earlier.[36]

4. Complexes of the type RTeX(S-S)$_2$

Six complexes will be discussed in this group. Their molecular structures are quite similar and they all have distorted pentagonal bipyramidal structures with axial aryl groups and weak intermolecular Te---X/S/C contacts representing the missing axial ligand. The molecules are thus loosely bonded into pairs. The equatorial group consists of TeS$_4$X where the sulfur atoms come from the two dialkyldithiocarbamate ligands. The main differences between the complexes are found in the different degree of rotation of the phenyl groups and also in the differences in intermolecular secondary bonding. The first such complex whose structure was solved was EtOPhTeCl(Et$_2$NCS$_2$)$_2$, **27**.[37] It is also the only one with X = Cl. The secondary intermolecular contacts, Te---S, are very long and weak with an average length of 3.722 Å, the sum of the respective van der Waals radii is 3.86 Å[38]. The corresponding average Te---S contact is 3.715 Å in PhTe(Et$_2$NCS$_2$)$_2$I, **28**. [39] In both **27** and **28** there are two crystallographically independent molecules in the unit cell. The next three complexes 4-MeOPhTeBr(Et$_2$NCS$_2$)$_2$,

29,[40] 4-MeOPhTe($Br_{0.4}I_{0.6}$)(Et_2NCS_2)$_2$, **30** [41] and 4-MeOPhTe-(Et_2NCS_2)$_2$I, **31**, [41] all have intermolecular Te---X contacts. Also **30** and **31** are isomorphous. The structure of **31** is shown in Figure 2e. The Te---X contacts are relatively stronger than the Te---S contacts in **27** and **28**. At 3.424, 3.476(Br) and 3.558(I), and 3.569 Å for **29**, **30**, **31**, respectively, they are on the average 0.445(Br) and 0.48(I) Å shorter than the respective van der Waals contacts.[38] The corresponding difference for the Te---S contacts in **27** and **28** is only 0.14 Å. The last complex in this group, 4-MeOPhTeBr(Me_2NCS_2)$_2$, **32**, [7] has an intermolecular axial Te---C π contact like the one found in **1**. In the RTeX(S-S)$_2$ complexes, the lone pair of electrons on Te is probably stereochemically inert. With no intermolecular associations, it would be expected to be located at the vacant axial position where it would screen possible donor atoms of neighbour molecules from the residual positive charge on Te.

5. Complexes of the type $RTeX_2$(S-S)

There are only two compounds in this group and both have the same type of structure. The similar compound, 4-MeOPhTeBr_2 [$(MeO)_2PS_2$] ,[42] was known previously. The compounds in this group have distorted octahedral structures. The sulfur and halogen atoms are equatorial, the aryl group is axial. The other axial position is occupied by one of the halogen atoms from a neighbour molecule. The resulting weak, secondary bonds tie the molecules together in pairs. In PhTeI_2(Et_2NCS_2), **33**, [43] there are three crystallographically independent molecules with very weak secondary Te---I bonds of 3.898(2), 4.192(1) and 4.233(1) Å. They may be compared to the sum of Pauling's and Bondi's van der Waals radii of 4.35 and 4.04 Å, respectively. [21, 38] The intermolecular secondary bonds are stronger in 4-MeOPhTe($Br_{0.4}I_{0.6}$)$_2$(Et_2NCS_2), **34**, [43] where Te----Br = 3.676(6) and Te---I = 3.872(3) Å. See also Figure 3a.

6. Complexes of the types R_2Te(S-S)$_2$ and R_2Te(S-O)$_2$

There are twelve compounds in this group with R being both alkyl and aryl groups. They all have strongly anisobidentate dithio ligands forming covalent and secondary intramolecular bonds. In addition there are also secondary intermolecular Te---S contacts in two of the complexes. If the secondary bonding is ignored, all complexes have a

ψ-trigonal bipyramidal structure, the socalled sawhorse structure, with two axial sulfur atoms, one from each sulfur containing ligand. The main difference between the structures lies in the orientation of the dithio ligands. In some complexes they are roughly coplanar, in addition the carbon bonded to Te from one of the R-ligands is close to this plane (Type 1). In the remainder, the planes of the two dithio ligands are roughly at right angles to each other, each being coplanar with one of the Te-C bonds (Type 2). See also Figures 3b and c which show the structures of **38** and **39**, respectively.

A. COMPLEXES $R_2Te(S\text{-}S)_2$

a. Compounds with R = Me	Compound no.	Str. type	Ref.
$Me_2Te(OCMe_2CMe_2OPS_2)_2$	**35**	2	44
$Me_2Te(OCH_2CEt_2CH_2OPS_2)_2$	**36**	2	44
$Me_2Te(EtOCS_2)_2$	**37**	1	45
$Me_2Te[CH_2(CH_2)_3NCS_2]$	**38**	1	46
$Me_2Te[CH_2(CH_2)_4NCS_2]$	**39**	2	46
$Me_2Te[CH_2(CH_2)_3NCS_2]\ [CH_2(CH_4)\ NCS_2]$	**40**	1	46
b. Compounds with R_2 = 			
 $Te[(EtO)_2\ PS_2](Et_2NCS_2)$	**41**	2	36
c. Compounds with R = Ph			
$Ph_2Te(EtOCS_2)_2$	**42**	2	45
$Ph_2Te(Ph_2PS_2)_2$	**43**	2	47
B. COMPLEXES $R_2Te(S\text{-}O)_2$			
a. Compounds with R = Me			
$Me_2Te(Et_2NCOS)_2$	**44**	1	48
$Me_2Te(i\text{-}PrOCOS)_2$	**45**	1	49
b. Compounds with R = Ph			
$Ph_2\,Te(i\text{-}PrOCOS)_2$	**46**	1	49

Of the twelve compounds listed above, half have a type 1 structure. By inclusion of the Te---S and Te---O intramolecular bonds, these compounds at first glimpse have a ψ-pentagonal bipyramidal structure with one carbon and the four sulfur atoms (or two sulfur and two oxygen atoms) in the equatorial plane while the other carbon atom and the lone pairs are axial. In **40**, **45** and **46** there is an additional intermolecular, secondary bond in an axial direction and this replaces the lone pair (axial) on Te(IV). Figure 3d shows the structure of **45**.

The remaining six compounds have a type 2 structure. Including the intramolecular secondary Te---S bonds, results according to

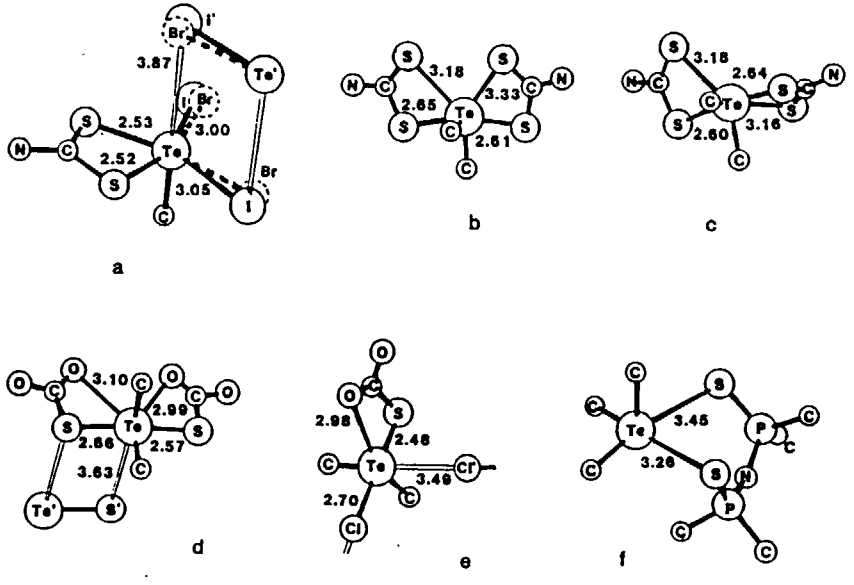

FIGURE 3. Structures of further Te(IV) compounds. a, 4-MeOPhTe($Br_{0.4}I_{0.6}$)$_2$(Et_2NCS_2), **34**; b, $Me_2Te[CH_2(CH_2)_3NCS_2]_2$, **38**; c, $Me_2Te[CH_2(CH_2)_4NCS_2]_2$, **39**; d, Me_2Te(i-PrOCOS)$_2$, **45**; e, Me_2TeCl(MeOCOS), **57**; f, $Ph_3Te[N(Ph_2PS)_2]$, **61**.

Drake *et al* in a distorted octahedral structure with an inert lone pair, however it may alternatively be described as ψ-pentagonal bipyramidal with a stereochemically active lone pair as postulated for compound **41**. It may be of interest to mention that in $Ph_2Te(i\text{-}Pr_2OCOS)_2$, **46**, it is the alcoxy oxygen that form the secondary intramolecular Te---O bond to one of the ligands while the carboxyl oxygen not bonded to Te forms the weak intermolecular Te---O contact [3.260(6) Å compared to 3.58 Å for a van der Waals contact].[38]

7. Complexes of the types $R_2TeX(S\text{-}S)$ and $R_2TeX(S\text{-}O)$

Ignoring secondary bonding, the structures of the compounds are all ψ-trigonal bipyramidal with an equatorial lone pair of electrons, *i. e.* the sawhorse structure found for the preceeding group of compounds. All molecules of the present group also have secondary intramolecular Te---S and Te---O bonds. Intermolecular secondary bonds Te---S, Te---O and Te---X are also common . Another common trait is that all have R = Me.

A. COMPLEXES $Me_2TeX(S\text{-}S)$

Compound	No	Ref.
$Me_2TeCl(EtOCS_2)$	**47**	50
$Me_2TeI(i\text{-}PrOCS_2)$	**48**	50
$Me_2TeCl[\overline{CH_2(CH_2)_3NCS_2}]$	**49**	46
$Me_2TeBr[\overline{CH_2(CH_2)_3NCS_2}]$	**50**	46
$Me_2TeI[\overline{CH_2(CH_2)_3NCS_2}]$	**51**	46
$Me_2TeCl[\overline{CH_2(CH_2)_4NCS_2}]$	**52**	46
$Me_2TeI[\overline{CH_2(CH_2)_4NCS_2}]$	**53**	46

B. COMPLEXES $Me_2TeX(S\text{-}O)$

Compound	No	Ref.
$Me_2TeCl(Et_2NCOS)$	**54**	48

$Me_2TeBr(Et_2NCOS)$	**55**	48
$Me_2Te(Et_2NCOS)I$	**56**	48
$Me_2TeCl(MeOCOS)$	**57**	49
$Me_2TeBr(i\text{-}PrOCOS$	**58**	49

There are intramolecular secondary Te---S or Te---O bonds in all the above compounds. In addition they all, except **47** and **48,** also have intermolecular secondary Te---S, Te---O or Te---X bonds. Including these secondary bonds in the coordination sphere of Te results in a distorted octahedral coordination for compounds **49 - 58.** These compounds are knit together either into dimers or chain polymers. Compounds **47** and **48** have no intermolecular bonds and their structures are ψ-octahedral where the lone pair of electrons on Te is *trans* to one of the methyl groups. In the other compounds (**49-58**) this lone pair is replaced by an intermolecular contact. Generally the intermolecular secondary bonds are weaker than the intramolecular ones. See also Figure 3e for the structure of **57.**

8. Complexes of the type $R_3Te(S\text{-}S)$

This group comprises five compounds. All Te-S bonds are very weak and range from 3.017 to 3.67 Å. Thus the compounds are probably somewhat ionic. All have R = Ph,. In the first, $Ph_3Te(Et_2NCS_2)$, **59**, [51] there are two different Te-S bonds, one relatively short with a bond length of 3.017(2) Å and the other a secondary bond of 3.607(4) Å. They may be compared to a corresponding van der Waals contact of 3.86 Å. [38.] Intermolecular strong secondary Te---S bonds [3.294(2) Å] involving the weakly bound sulfur atom tie the molecules into pairs, giving an overall distorted octahedral coordination for Te, where the three phenyl groups are in a facial set *trans* to the three weakly bonded sulfur atoms. These weak, long Te---S bonds may also be interpreted in terms of the strong *trans* influences of the phenyl groups. The lone electron pair of Te may well point in between the long Te---S bonds making the structure ψ-monocapped octahedral.

Three examples of purely monomeric complexes have been studied by Haiduc et al [52] and by Wieber et al [28] . They are $Ph_3Te(Ph_2PS_2)$, **60**,[52] $Ph_3Te[N(SPPh_2)_2]$, **61**[52] and $Ph_3Te[(EtO)_2PS_2]$,

62.[28] The two thiolato ligands are somewhat anisobidentate, especially in **60** where the Te---S bond lengths are 3.331 and 3.655 Å. These bonds are in directions roughly *trans* to two of the phenyl ligands and the coordination sphere around Te may then be classified as y-octahedral. In **61** (Figure 3f) with the wide bite ligand tetraphenyldithio-imidodiphosphinate, the structure is similar, but more regular. The two Te---S secondary bonds are again *trans* to two phenyl groups.

The last compound in this group is the dimeric bis(triphenyl-tellurium)hexasulfide, $(Ph_3Te)_2S_6$, **63**.[53]. Here both end atoms (S1 and S2) of the S_6^{2-} anion bridges the two tellurium atoms forming two secondary Te---S bonds to each tellurium atom ranging in length from 3.123(8) - 3.342(9) Å. From the upper part of the S_6^{2-} anion, S3---Te1 and S4---Te2 secondary bonds are formed. The result is an irregular octahedral structural environment of tellurium similar to that of **60**.

Conclusion

Many new tellurium compounds have been described here. For Te(II), the tendency, to form four-coordinate square planar or trapezoid planar complexes is a typical trait. Only with ligands with strong *trans* influences like aryl, which virtually expels a ligand *trans* to itself, do we find three-coordinate T-shaped structures. The two sterically active lone pairs of electrons are located on both sides of the coordination plane and this causes a fifth ligand to attach itself to Te in this plane rather than at right angles to it.[2] In ref. 5 we have shown that a ligand's capability to delocalize positive charge from tellurium strengthen the Te-L bond and increase L's *trans* influence in a 3c - 4e systems.

For Te(IV) compounds described here, the ψ-octahedral, octahedral, ψ-pentagonal bipyramidal and pentagonal bipyramidal geometries predominate. Secondary bonding is included in the description of the structures and is most common among Te(IV) compounds with halogen and chalcogen containing ligands. The stereochemical activity of the lone pair varies among the Te(IV) compounds, and is often reduced by secondary bonding.

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