

Stereochemical Aspects of Tellurium Complexes with Sulfur Ligands: Molecular Compounds and Supramolecular Associations

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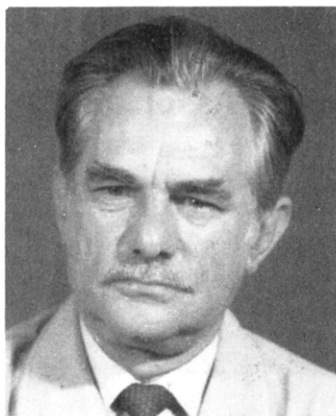
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A. Introduction

1. Bonding in Tellurium Complexes

Tellurium is known to display various oxidation states (-2, +2, +4, and +6 being the most common) and coordination numbers (from two to eight). This leads to a great variety of compositions and structures. With "soft" atoms like sulfur, tellurium seems to prefer low oxidation states, and only with highly electronegative elements and "hard" donors, like oxygen and fluorine, does tellurium exhibit the maximum +6 oxidation state.

This review covers the compounds in which tellurium is coordinated by at least one ligand containing a sulfur donor site, with particular emphasis on compounds in which two or more tellurium-sulfur bonds are present in the molecule. Monodentate sulfur ligands, in particular thiourea and its derivatives, have been relatively



Ionel Haiduc was born in Cluj, Romania, in 1937 and graduated in chemistry at the University of Cluj in 1959. He received his Ph.D. with Prof. K. A. Andrianov in Moscow, Russia, with a dissertation on organosilicon ring compounds. In 1966 he received a Fulbright fellowship which enabled him to carry out post-doctoral research with Prof. Henry Gilman at Iowa State University, Ames, IA. He spent another year and a half as a post-doctoral fellow with Prof. R. Bruce King at the University of Georgia in 1971–1972. Since 1973 he has been a full professor of inorganic chemistry at Babeş-Bolyai University in Cluj-Napoca, Romania. Prof. Ionel Haiduc published his first book on inorganic ring systems in Romanian in 1960 and more recently has published books entitled *The Chemistry of Inorganic Ring Systems* (1970), *The Chemistry of Inorganic Homo- and Heterocycles* (co-edited with D. B. Sowerby, 1987), *Basic Organometallic Chemistry* (with J. J. Zuckerman, 1985), and *Organometallics in Cancer Chemotherapy* (with C. Silvestru, 2 volumes, 1989, 1990). His research interests cover inorganic ring systems, organometallic chemistry of main group elements with particular emphasis on organophosphorus ligands, biologically active main group organometallics, and supramolecular organometallic chemistry. Prof. Haiduc has received visiting grants from the National Science Foundation (United States, October, 1992) and the European Community (Spain, Fall 1993) and is currently a visiting research professor at the Instituto de Química, Universidad Nacional Autónoma de México. After the anticommunist revolution in Romania (December, 1989) Prof. Haiduc was elected rector (president) of Babeş-Bolyai University and in 1991 full member of the Romanian Academy.

well investigated structurally^{1–3} and their geometry reflects the bonding abilities of tellurium. With bidentate 1,1-dithiolato ligands displaying a small bite, such as dithiocarbamates, xanthates, and dithiophosphates, the structure is influenced by the coordinating ability of the ligand, and strong distortions are observed in comparison with the monodentate sulfur ligands, even if the main features of tellurium coordination are maintained. Thus, for example, the regular square planar geometry observed with monodentate sulfur ligands, like thiourea, becomes trapezoidal planar with small bite bidentate ligands.

Another factor which has to be considered is the presence of lone electron pairs on tellurium. Such lone electron pairs may become stereochemically active, and thus influence the coordination geometry in a significant manner. In lower oxidation states and coordination numbers, lone pairs are generally stereochemically active. In higher oxidation states and in compounds with higher coordination numbers (e.g. 8, corresponding to a bisdisphenoidal or D_{2d} dodecahedral coordination geometry), the lone pair of tellurium(IV) is difficult to locate and appears to be stereochemically inactive. The stereochemical inactivity of the lone pair may be understood to mean it does not occupy a vertex in the coordination polyhedron although it may well be antibonding and thus weaken the tellurium–ligand bond.



R. Bruce King was born in Rochester, NH, in 1938, attended Oberlin College (B.A. 1957), and was an NSF Predoctoral Fellow with Prof. F. G. A. Stone at Harvard University (Ph.D. 1961). After a year at du Pont and four and half years at the Mellon Institute he joined the faculty of the University of Georgia where he is now Regents' Professor of Chemistry. His research interests range from synthetic organometallic and organophosphorus chemistry to applications to topology and graph theory in inorganic chemistry and the inorganic chemistry of nuclear waste treatment. Prof. King has been the American Regional Editor of the *Journal of Organometallic Chemistry* since 1981 and is Editor-in-Chief of the *Encyclopedia of Inorganic Chemistry* scheduled for publication in Summer 1994. He is the recipient of American Chemical Society Awards in Pure Chemistry (1971) and Inorganic Chemistry (1991). He recently published a book entitled *Applications of Graph Theory and Topology in Inorganic Cluster and Coordination Chemistry* (1993) and has just completed a book on *Inorganic Main Group Element Chemistry* scheduled for publication later in 1994.



M. Gary Newton was born in Millen, GA, in 1939, attended the Georgia Institute of Technology (B.S. 1961, Ph.D., 1965). His doctoral adviser was Prof. James R. Cox, currently at the University of Houston. He then spent two years as a post-doctoral trainee in single-crystal X-ray diffraction with Prof. Ian C. Paul at the University of Illinois at Urbana-Champaign. In 1969, he joined the faculty of the University of Georgia where he is now Associate Professor of Chemistry. His primary research interests include structural studies of diterpene alkaloids, organophosphorus compounds, and transition metal organometallic compounds.

The bonding between tellurium and sulfur presents some peculiarities when interatomic distances are considered. In addition to bonds whose length corresponds to the sum of accepted covalent radii, somewhat longer bonds are frequently observed. These are considered as three-center four-electron bonds, formed by the use of a single p orbital of tellurium to form two covalent bonds.^{1,2,4} In addition, secondary bonds or semibonds, significantly longer than the covalent bonds but shorter than the sum of the van der Waals radii,⁵ also occur in many tellurium–sulfur complexes.

Table 1. Atomic Radii of Tellurium and Sulfur and the Corresponding Tellurium–Sulfur Distances, Å

atomic radii	element		Te–S	ref
	Te	S		
covalent (2c-2e)	1.356	1.020	2.376	9
covalent (2c-2e)	1.37	1.04	2.41	10
three-center (3c-4e)	1.64			4
nonbonded ^a	1.75	1.60	3.35	10, 11
van der Waals	2.20	1.85	4.05	12
van der Waals	2.06	1.80	3.86	13
van der Waals	1.91	1.68	3.59	4

^a Measuring the limiting nonbonded E...E distances for an EE' pair connected by an E–M–E angle.^{9,10}

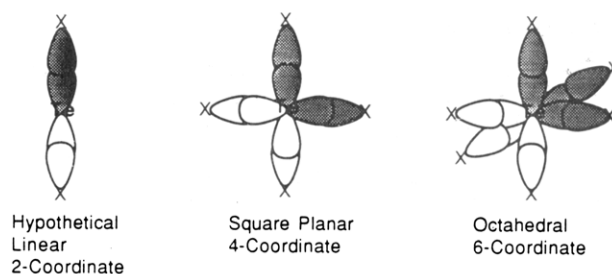
In Table 1 the atomic radii of tellurium and sulfur for covalent, three-center four-electron bonds and nonbonded van der Waals interactions and the corresponding tellurium–sulfur distances estimated from these values are given, to serve as basis for comparisons with the interatomic distances actually observed in various tellurium–sulfur compounds structurally investigated. Thus, in linear S–Te–S systems, when the interatomic distances are longer than expected for covalent normal two-center two-electron (2c-2e) bonds, a three-center four-electron (3c-4e) bond is assumed to be present (Figure 1). For a tellurium–sulfur bond in a three-center system around tellurium, the expected length is equal to the sum of the 3c-4e radius of tellurium (1.64 Å) and the covalent radius of sulfur (1.04 Å), i.e. 2.68 Å. Values close to this are frequently found in the tellurium compounds to be discussed in this review. If the sulfur ligands display nonidentical *trans* influence, this induces an asymmetry in the 3c-4e system. In C–Te–X (halogen) systems, the pure 2c-2e Te–C bond has a strong *trans* influence and reduces the tellurium–halogen interaction to a van der Waals contact or a very weak secondary interaction. (See examples below.) In the S–Te–X (halogen) sequence there is an intermediate situation corresponding to a clearly asymmetric 3c-4e bond. Thus since the sulfur ligands have a greater *trans* influence, the Te–S bond is strengthened and the Te...X bond is weakened being frequently reduced to a secondary interaction although shorter than a van der Waals contact. An example is the compound *cis*-Te(tu)₂I₂, in which the S–Te–I sequence is a 3c-4e system with Te–S 2.521 Å and Te...I 3.162 Å. Comparison with the sum of covalent radii (Te–S 2.38 Å and Te–I 3.00 Å) reveals that the Te–S bond is 0.14 Å longer than the 2c-2e covalent bond and the Te–I bond is 0.16 Å longer. The total length of the S–Te–I 3c-4e system is found to be

$$d(\text{Te–S}) + d(\text{Te...I}) = 2.521 + 3.162 = 5.683 \text{ \AA}$$

which is in good agreement with the calculated value of

$$2r(\text{Te}_{3c-4e}) + r(\text{S}_{\text{cov}}) + r(\text{I}_{\text{cov}}) = (2)(1.64) + 1.04 + 1.33 = 5.65 \text{ \AA}$$

In square planar complexes two perpendicular three-center bonds explain the structure (Figure 1). In addition, octahedral complexes, formed by three perpendicular three-center four-electron bonds, are possible. In all of these geometries (linear, square planar, and octahedral) longer bonds than covalent ones have

**Figure 1.** Three-center four-electron (3c-4e) bonding in linear, square planar, and octahedral tellurium complexes.

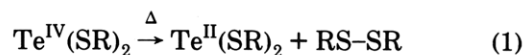
been observed with monodentate ligands. In the case of small bite chelating bidentate ligands, the situation is not so straightforward, and the small ligand bite may (and does) produce distortions. There is some disagreement as to the values of the van der Waals radii, but even the shortest van der Waals Te...S interatomic distance suggested (3.59 Å)⁴ is significantly longer than the secondary interactions observed in many tellurium–sulfur complexes. Probably the estimated van der Waals radius of sulfur taken as 1.68 Å in this reference is too small and leads to an underestimated value for the van der Waals Te...S distance of 3.56 Å.

A direct result of the three-center four-electron bonds is the strong *trans* influence of some groups (e.g. organic substituents like phenyl) attached to tellurium. This *trans* influence leads to a dramatic lengthening of a bond across from the given substituent. In this case a ligand that overlaps more efficiently with the tellurium p orbital involved in the 3c-4e bond, weakens the bond *trans* to itself if the latter has a smaller overlap. This weakening may end up in complete expulsion of the *trans* ligand leading, for example, to the transformation of a square planar complex into a T-shaped complex.

In certain tellurium complexes, in particular in those which tellurium displays a higher oxidation state and not the highest coordination numbers (e.g. four- or five-coordinate Te^{IV} complexes), the VESPR theory operates.^{6,7} This means that the lone electron pairs should be taken into account in explaining the observed geometry of the complexes.⁸

2. Organization of the Review

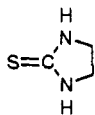
In accord with the features of the structural chemistry of tellurium–sulfur complexes as outlined above, complexes of monodentate ligands will be discussed first followed by complexes with chelating bidentate ligands. The order of presentation will start with tellurium in the highest oxidation state (+4 in sulfur complexes) and with the highest coordination number. This procedure was chosen because quite frequently lower oxidation states appear as a result of intramolecular redox reactions in which tellurium is reduced by the coordinated ligand with elimination of the corresponding disulfide (the oxidation product of the coordinated ligand) with corresponding reduction of the tellurium coordination number. This can be schematically represented as follows:



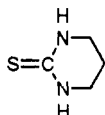
Thus, the structures of tellurium complexes can be correlated with their frequently observed chemical transformations.

3. Abbreviations

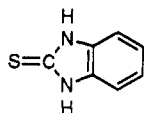
VSEPR	valence shell electron pair repulsion (theory)
L or S	monodentate sulfur ligand in figures
S-S	bidentate sulfur ligand
tu	thiourea, $\text{S}=\text{C}(\text{NH}_2)_2$
tmtu	tetramethylthiourea, $\text{S}=\text{C}(\text{NMe}_2)_2$
dmtu	dimethylthiourea, $\text{S}=\text{C}(\text{NHMe})_2$
etu	ethylenethiourea,



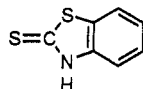
trtu trimethylenethiourea,



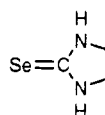
phtu phenylenethiourea, 1*H*-benzimidazole-1-thione,



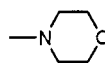
bztlit 2,3-dihydrobenzothiazole-2-thione,



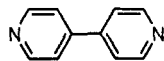
su selenourea, $\text{Se}=\text{C}(\text{NH}_2)_2$
etsu ethyleneselenourea,



morph morpholyl,



4,4'-bipy 4,4'-bipyridine,



dte dithiocarbamate
Me methyl
Et ethyl
Pr propyl
Prⁱ isopropyl
Bu *n*-butyl
Ph phenyl

B. Tellurium-Sulfur Complexes of Monodentate Ligands

1. Tellurium(IV) Complexes

a. Six-Coordinate, Octahedral Complexes with TeS_2X_4 Units

This class of compounds comprises tellurium tetrahalide complexes with the monodentate ligands tet-

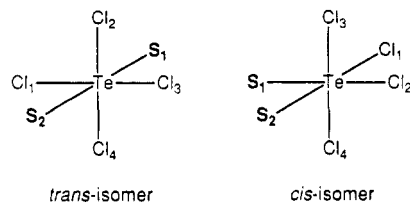


Figure 2. Stereoisomers of six-coordinate tellurium complexes with TeS_2X_4 structural units.

ramethylthiourea (tmtu),^{14,15} 2,3-dihydrobenzothiazole-2-thione (bztlit),¹⁶ and 1*H*-benzimidazole-1-thione (phtu).¹⁷ The complexes display distorted octahedral geometries, in which two sulfur atoms occupy *trans* or *cis* positions (Figure 2 and Table 2). The Te-S bonds are longer than expected for covalent bonds, thus suggesting 3c-4e bonding. Angular distortions of the octahedral axes cannot be assigned to constraints imposed by the small bites of the ligands (such as happens with bidentate ligands). The large S-Te-Cl angle of 105.94° observed in $[\text{Te}(\text{tmtu})_2\text{Cl}_4]$ ¹⁴ may therefore indicate lone-pair activity.¹⁸ Thus, in this compound the *trans*-axial (orthogonal) atoms are closer to colinearity than in bidentate ligand complexes, and the opening of the S-Te-Cl angle is the major distortion. With the exception noted, the interaxial bond angles are remarkably close to 90°.

2. Tellurium(II) Complexes

a. Four-Coordinate, Square Planar Complexes with TeS_4 Units

A large number of tellurium(II) complexes with monodentate ligands forming square planar TeS_4 coordination units have been investigated. Most of them are derivatives of thiourea or substituted thioureas.¹⁷⁻³⁴ The complexes are mostly centrosymmetric (Figure 3) with exactly planar geometry, but some distortions are induced when two different sulfur ligands are coordinated, e.g. a thiourea and an alkanethiosulfonate or a thiocyanato group. Mixed $\text{TeS}_2\text{S}'_2$ ligand complexes are in general *trans* complexes.

The interatomic distances and bond angles are listed in Table 3. The Te-S bond lengths are obviously longer than 2c-2e bonds; thus, the complexes seem to be formed through two perpendicular 3c-4e systems.

In some cases the four-coordinate TeS_4 unit is the result of dimerization of TeS_3 groups, with sulfur atoms shared by two square planar units, as shown in Figure 4. In these dinuclear complexes of general composition

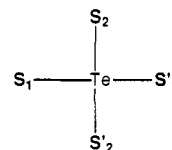


Figure 3. Tellurium(II) complexes with planar TeS_4 coordination units.

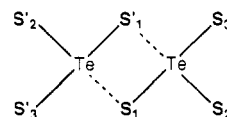
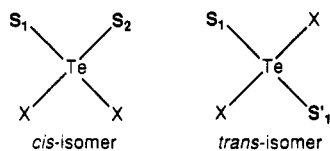


Figure 4. Four-coordinate TeS_4 units from the dimerization of TeS_3 groups.

Table 2. Molecular Dimensions in Six-Coordinate, Octahedral $\text{Te}^{\text{IV}}\text{L}_2\text{X}_4$ Complexes with TeS_2X_4 Units

compound	bond lengths, Å		bond angles, deg	ref
	Te-S	Te-X		
<i>trans</i> -Te(tmtu) ₂ Cl ₄ monoclinic ^a	Te-S ₁ 2.726 Te-S ₂ 2.649	Te-Cl ₁ 2.455 Te-Cl ₂ 2.530 Te-Cl ₃ 2.601 Te-Cl ₄ 2.544	transaxial: S ₁ -Te-S ₂ 174.06 Cl ₁ -Te-Cl ₃ 172.07 Cl ₂ -Te-Cl ₄ 177.27 perpendicular: Cl ₁ -Te-Cl ₂ 89.44 Cl ₂ -Te-Cl ₄ 91.28 Cl ₂ -Te-S ₁ 88.71 Cl ₂ -Te-Cl ₃ 90.53 Cl ₃ -Te-Cl ₄ 89.14	14
<i>trans</i> -Te(tmtu) ₂ Cl ₄ orthorhombic ^b	Te-S ₁ 2.699	Te-Cl ₁ 2.536 Te-Cl ₂ 2.520	perpendicular: S ₁ -Te-Cl ₂ 98.5 S ₁ -Te-Cl ₃ 91.1 Cl ₂ -Te-Cl ₃ 90.9	15
<i>trans</i> -Te(tmtu) ₂ Br ₄	Te-S ₁ 2.707	Te-Br ₁ 2.707 Te-Br ₂ 2.686	perpendicular: S ₁ -Te-Br ₂ 98.7 S ₁ -Te-Br ₃ 90.6 Br ₃ -Te-Br ₄ 90.8	15
<i>trans</i> -Te(bztl _t) ₂ Cl ₄	Te-S ₁ 2.704	Te-Cl ₁ 2.509 Te-Cl ₂ 2.502	perpendicular: Cl ₁ -Te-Cl ₂ 88.8 Cl ₁ -Te-S ₁ 89.9 Cl ₂ -Te-S ₁ 92.4 S ₁ -Te-S ₂ 87.3	16
<i>cis</i> -Te(phtu) ₂ Cl ₄	Te-S ₁ 2.630	Te-Cl ₁ 2.525 Te-Cl ₂ 2.559	transaxial: S ₁ -Te-Cl ₂ 178.3 perpendicular: S ₁ -Te-S ₂ 87.3 Cl ₁ -Te-S ₁ 91.2 Cl ₁ -Te-Cl ₂ 87.6	17

^a Formed from the orthorhombic form on prolonged storage. Note that the molecule is not centrosymmetric like the orthorhombic form.¹⁶ ^b Centrosymmetric molecule.

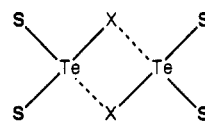
**Figure 5.** Square-planar TeS_2X_2 complexes (*cis* and *trans* isomers).

$[\text{Te}_2\text{L}_6]\text{X}_4$ some distortions are observed, since the terminal Te-S bonds become shorter, even close to the length expected for normal covalent (2c-2e) bonds, while the bridging Te-S bonds are longer, but still remain in the range of covalent bonding. The presence of shorter (terminal) and longer (bridging) Te-S bonds reduces the symmetry of the coordination unit.

The known representatives of this type of coordination are thiourea (tu), ethylenethiourea (etu), and trimethylenethiourea (trtu) cationic complexes,³⁷⁻³⁹ with the anion outside of the coordination sphere. Their molecular dimensions are listed in Table 4.

b. Four-Coordinate Complexes with TeS_2X_2 and TeSX_3 ($\text{X} \neq \text{S}$) Units

These unsymmetrically substituted *cis*^{36,40-42} and *trans*^{21,30,40,43-45} square planar complexes (Figure 5) maintain the general features of the four-coordination geometry, but a slight distortion (asymmetry) is induced by the presence of two different donor atoms. The structural data for the complexes investigated are collected in Table 5. In *cis* complexes the Te-S bond lengths (perpendicular to each other) indicate strongly asymmetric 3c-4e bonding (*trans* influence). In the *cis* complexes the sulfur-containing ligand is mostly located *trans* to the halogen and has a greater *trans* influence.

**Figure 6.** Dinuclear tellurium complexes with planar coordinated tellurium.

In the resulting S-Te-X 3c-4e system, the Te-S bond is relatively short while the Te-X bond is lengthened. In *trans* complexes the 3c-4e Te-S bonds are more nearly symmetric.

Some halogenothioureatellurium complexes associate through covalent halogen bridges.⁴⁶⁻⁴⁸ Thus, dinuclear complexes, e.g., $[\text{Te}_2(\text{etu})_4\text{Br}_2]\text{Br}_2$, with trapezoidal planar units connected through halogen double bridges are formed, which also leads to a TeS_2X_2 coordination environment (Figure 6). In these complexes the tellurium-sulfur bonds are terminal and, in agreement with previous observations, are part of a strongly asymmetric 3c-4e system, as shown by the corresponding interatomic distances (Table 6).

Two tellurium(II) compounds with ethylenethiourea and bromine, of unusual compositions $\text{Te}_2(\text{etu})_4\text{Br}_4$ ⁴⁶ and $\text{Te}_7(\text{etu})_{12}\text{Br}_{16}$ ⁴⁹ have been prepared. The former compound contains a dinuclear cation of the type just described and can be written as an ionic complex $[(\text{etu})_2\text{Te}(\mu\text{-Br})_2\text{Te}(\text{etu})_2]^{2+}2\text{Br}^-$. The molecular dimensions of the two polymorphic forms, orthorhombic and monoclinic, are listed in Table 6. The halogen bridges are elongated, as mentioned above, and the coordination sphere is less symmetric than a perfect square planar one. The sulfur atoms are in *cis* positions. The structure of the second compound, $\text{Te}_7(\text{etu})_{12}\text{Br}_{16}$, as established by X-ray diffraction, is best described

Table 3. Molecular Dimensions in Four-Coordinate, Square Planar Compounds with TeS₄ Units

compound	bond lengths, Å		bond angles, deg: S ₁ -Te-S ₂	ref
	short Te-S ₁	long Te-S ₂		
a. Type TeL ₄ (Four Identical Sulfur Ligands)				
[Te(tu) ₄][HF ₂] ₂	2.670	2.697	90.76	19
[Te(tu) ₄]Cl ₂	2.685	2.690	90.60	20
[Te(tu) ₄]Cl ₂	2.632	2.726	88.32	19
[Te(tu) ₄]Cl ₂ ·2H ₂ O	2.677	2.688	90.3	20
[Te(tu) ₄]Cl ₂ ·2H ₂ O	2.681	2.687	89.71	19
[Te(tu) ₄](ClO ₄) ₂	2.573	2.638	90.7	21
	2.707	2.845		
[Te(tu) ₄](ClO ₄) ₂	2.649	2.716	91.16	19
	2.654	2.843		
[Te(dmtu) ₄]Cl ₂	2.674	2.690	88.8	21, 22
[Te(etu) ₄]Cl ₂	2.666	2.681	91.06	23
[Te(etu) ₄]Cl ₂ ·2H ₂ O	2.654	2.702	88.8	24
	2.609	2.737	90.2	
[Te(etu) ₄][TeCl ₆]	2.627	2.735	86	25
[Te(trtu) ₄]Cl ₂ ·2H ₂ O	2.680	2.684	87.20	19
[Te(trtu) ₄](ClO ₄) ₂	2.667	2.701	89.82	19
[Te(phtu) ₄]Cl ₂	2.674	2.678	90.5	26
[Te(phtu) ₄][ClO ₄] ₂ ·6H ₂ O	2.666	2.675	88.7	27
b. Type TeL ₂ L' ₂ (Two Different Sulfur Ligands)				
<i>trans</i> -[Te(tu) ₂ (tmtu) ₂]Cl ₂	2.710	2.688	91.37	28
<i>trans</i> -[Te(tu) ₂ (tmtu) ₂]Br ₂	2.706	2.679	91.45	28
<i>trans</i> -[Te(tu) ₂ (phtu) ₂]Cl ₂	2.694	2.685	89.4	29
<i>trans</i> -Te(tu) ₂ (SSO ₂ Me) ₂	2.667	2.684	90.6	30
<i>trans</i> -Te(tmtu) ₂ (SCN) ₂	2.691	2.685	92.10	23
<i>trans</i> -Te(tmtu) ₂ (SSO ₂ Ph) ₂	2.724	2.657	100.5, 79.5 ^a	31
<i>trans</i> -[Te(etu) ₂ (SCN) ₂] ₂	2.651	2.684	90.1	32
<i>trans</i> -Te(etu) ₂ (SSO ₂ Me) ₂	2.663	2.694	91.6	33 (tricl)
<i>trans</i> -Te(etu) ₂ (SSO ₂ Me) ₂	2.687	2.685	92.6	33 (monocl)
<i>trans</i> -Te(etu) ₂ (SSO ₂ Ph) ₂	2.713	2.686	90.8	34
<i>trans</i> -Te(trtu) ₂ (SSO ₂ Ph) ₂	2.691	2.668	88.85	35
<i>cis</i> -Te(etu) ₂ (SCN) ₂	2.515	2.885	92.22	36
	2.520	2.947		
<i>cis</i> -Te(trtu) ₂ (SCN) ₂	2.530	2.867	94.01	36

^a This compound shows "abnormal" deviations (~10°) from the true square planar values for the bond angles observed in other complexes. This is explained by strain *within* the molecule rather than crystal packing effects.

Table 4. Molecular Dimensions of Dinuclear [Te₂L₆]⁴⁺ Derivatives

compound	Te-S bond lengths, Å				bond angles, deg: S _{ter} -Te-S _{br}		ref
	bridging		terminal				
	Te-S ₁	Te-S ₁	Te-S ₂	Te-S ₃			
[Te ₂ (tu) ₆][HF ₂] ₄	2.840	3.017	2.481	2.547	176.24		37
[Te ₂ (etu) ₆][HF ₂] ₄	2.857	3.06	2.469	2.532	174.6	172.6	38
[Te ₂ (etu) ₂][ClO ₄] ₄	2.860	2.928	2.507	2.525	175.97	175.59	39
[Te ₂ (trtu) ₆][ClO ₄] ₄ ^a	2.816	2.956	2.493	2.545	177.0	177.82	39
[Te ₂ (trtu) ₆][ClO ₄] ₄ ^a	2.827	3.040	2.441	2.543	164.24	170.39	39

^a Two isomers differing by orientation of the trtu ligands.

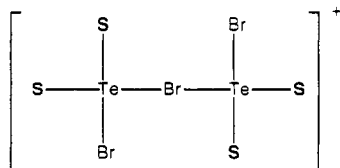


Figure 7. The environment of the tellurium atoms in the binuclear cation [(etu)₂BrTe(μ-Br)TeBr(etu)₂]⁺.

by the formula {[(etu)₂BrTe(μ-Br)TeBr(etu)₂]⁺}₃Br⁻[TeBr₆]²⁻ and contains terminal and bridging bromine atoms, free Br⁻ anions, and octahedral [TeBr₆]²⁻ anions.⁴⁹ The environment of the tellurium atoms in [(etu)₂BrTe(μ-Br)TeBr(etu)₂]⁺ is depicted in Figure 7 and selected interatomic distances and bond angles are listed in Table 7.

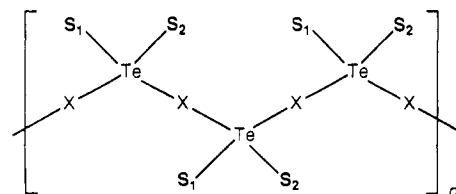


Figure 8. The environment of the tellurium atoms in polymeric [(trtu)₂Te(μ-Br)]_n.

Another compound of unusual composition, Te₃(trtu)₄Br₈ (trtu = trimethylenethiourea), is a polymer containing square planar [(trtu)₂Te(μ-Br)] units (Figure 8) connected through bromine bridges to form long chains.⁴⁹ The complex also contains anionic [TeBr₆]²⁻ groups and can be best written as {[Te(trtu)₂(μ-Br)]₂-

Table 5. Molecular Dimensions of Square Planar *cis*- and *trans*-TeS₂X₂ Derivatives

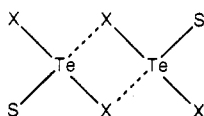
compound	bond lengths, Å		bond angles, deg				ref
	Te-S	Te-X	S-Te-S	vicinal S-Te-X	transaxial S-Te-X	X-Te-X	
a. <i>Cis</i> Complexes							
<i>cis</i> -Te(tu) ₂ Cl ₂	2.48	2.92	92.8	87.8	172.3	92.6	40
<i>cis</i> -Te(tu) ₂ Cl ₂	2.457	2.936	88.37	88.37	172.50	92.59	41
<i>cis</i> -Te(tu) ₂ Br ₂	2.47	3.05	95.0	86.7	172.2	93.0	40
<i>cis</i> -Te(tu) ₂ Br ₂	2.476	3.038	88.13	88.13	171.73	93.0	41
<i>cis</i> -Te(tu) ₂ I ₂	2.521	3.162	87.79	87.79	171.92	93.96	41
<i>cis</i> -Te(tu) ₂ (SeCN) ₂	2.458	3.039	103.10	82.65	170.68	92.65	36
<i>cis</i> -Te(trtu) ₂ Cl ₂	2.465	2.964	94.18	86.55		95.0	42
<i>cis</i> -Te(trtu) ₂ Br ₂	2.499	2.994	89.12	87.71		96.24	42
<i>cis</i> -Te(trtu) ₂ (SeCN) ₂	2.592	2.872	92.80	90.29	175.29	86.86	36
<i>cis</i> -Te(SCN) ₂ (su) ₂	2.536	3.165	101.96	82.11	167.93	96.24	36
<i>cis</i> -Te(SCN) ₂ (etsu) ₂	2.610	2.979	92.50	92.17	175.95	85.43	36
	2.607	3.025					
b. <i>Trans</i> Complexes							
<i>trans</i> -Te(tmtu) ₂ Cl ₂	2.687	2.586		88.69			43
	2.683	2.582					
<i>trans</i> -Te(tmtu) ₂ Br ₂	2.685	2.740		88.55			43
	2.685	2.734					
<i>trans</i> -Te(tmtu) ₂ I ₂	2.693	2.954		89.91			43
(triclinic)	2.687	2.962					
<i>trans</i> -Te(tmtu) ₂ I ₂	2.699	2.950	177.29	92.04			43
(monoclinic I)							
<i>trans</i> -Te(tmtu) ₂ I ₂	2.765	2.934		90.07			43
(monoclinic II)	2.637	2.978					
<i>tr</i> -Te(tmtu) ₂ (SeCN) ₂	2.728	2.815		91.61			44
<i>trans</i> -Te(etu) ₂ Br ₂	2.657	2.765		89.2			42, 45
	2.656	2.764		89.19			23
<i>trans</i> -Te(etu) ₂ I ₂	2.686	2.956		89.2			45
	2.671	2.2955		89.15			23
<i>tr</i> -Te(etu) ₂ (SeCN) ₂	2.676	2.809		89.9			32
<i>tr</i> -Te(trtu) ₂ (SeCN) ₂	2.670	2.834		89.73			44

Table 6. Molecular Dimensions of [Te₂(etu)₄Br₂]²⁺ Complexes

compound	bond lengths, Å		bond angles, deg					ref
	Te-S	Te-Br	<i>trans</i> S-Te-Br	<i>cis</i> S-Te-Br	S-Te-S	Br-Te-Br	Te-Br-Te	
[Te ₂ (etu) ₄ Br ₂]Br ₂ orthorhombic	2.495	3.042	175.75	92.54	90.73	84.32	95.68	46
[Te ₂ (etu) ₄ Br ₂]Br ₂ monoclinic	2.491	3.079	178.68	96.23	92.70	84.74	93.93	46
	2.481	3.015	170.51	86.39			96.60	

Table 7. Molecular Dimensions in the Cations Present in "Te₇(etu)₁₂Br₁₆" and "Te₃(trtu)₄Br₈"

cation	bond lengths, Å		bond angles, deg	ref
	Te-S	Te-Br		
[Te ₂ (etu) ₄ Br ₃] ⁺ in "Te ₇ (etu) ₁₂ Br ₁₆ "	2.477	2.966 (terminal)	S ₁ TeS ₂ 89.66	49
	2.491	3.036 (bridging)	BrTeBr 92.60	
{[Te(trtu) ₂ (μ-Br)] ⁺ } _n in "Te ₃ (trtu) ₄ Br ₈ "	2.468	3.065 (bridging)	S ₁ TeBr(μ) 174.71	49
	2.475	3.099 (terminal)	S ₁ TeS ₂ 92.29	
			BrTeBr 89.46	
			STeBr 177.53	
		TeBrTe 111.64		

Figure 9. The environment of the tellurium atoms in Te₂-(tmtu)₂X₄ derivatives.

[TeBr₆]_n. The essential molecular dimensions are listed in Table 7.

A coordination geometry of the type TeSX₃ was found in the dimeric complexes of the type Te₂(tmtu)₂X₄ (X = Cl, Br, I).^{47,48} This environment is the result of dimerization through halogen bridges. The two halves of the dimeric molecule (Figure 9) are related by a symmetry center. Each half consists of a T-shaped

STeX₂ unit, forming a third, longer Te...X bridge with the halogen *trans* to the sulfur. The geometry around tellurium is distorted square planar.^{47,48} The interatomic distances and bond angles are given in Table 8.

c. Three-Coordinate, T-Shaped Complexes with RTeS₂ and RTeSX Units

These complexes can be regarded as distorted square planar (T-shaped) originating from four-coordinate complexes by removal of a coordination site (Figure 10). In RTeS₂ complexes two sulfur atoms of a monodentate ligand are coordinated *trans* to each other, forming a nearly linear STeS group. The interatomic distances suggest 3c-4e bonding in this system. In known compounds the third coordination site, per-

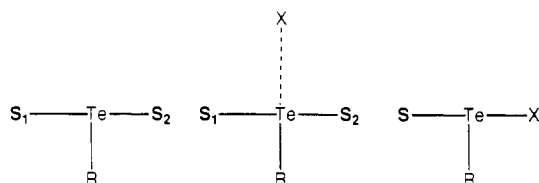
Table 8. Molecular Dimensions in Dimeric [Te^{II}LX(μ-X)]₂ Compounds

compound	bond distances, Å			bond angles, Å						ref(s)
	Te-S	Te-X _t	Te...X _b	S-Te...X _b	S-Te-X _b	X _b -Te-X _t	X _b -Te-X _b	X _t -Te...X _b	Te-X _b -Te	
Te ₂ (tmtu) ₂ Cl ₄	2.425	2.591 2.596	3.217	171.64	88.51	178.23	81.92	99.76	98.08	47, 48
Te ₂ (tmtu) ₂ Br ₄	2.441	2.703 2.769	3.284	173.18	89.61	178.0	82.86	97.15	97.14	47, 48
Te ₂ (tmtu) ₄ I ₄	2.473	2.899 3.017	3.360	175.19	91.11	176.02	84.29	93.15	95.71	48

Table 9. Molecular Dimensions in T-Shaped [RTe^{II}L₂]⁺ and [RTe^{II}LX] Derivatives

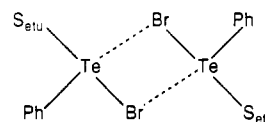
compound	bond lengths, Å		bond angles, deg			ref(s)
	Te-S ₁	Te-S ₂ or Te-X	RTeS ₁	RTeS ₂ or RTeX	S ₁ TeS ₂ or STeX	
a. RTeL ₂ Derivatives		Te-S ₂		R-Te-S ₂		
[Me ₄ N][PhTe(SCN) ₂]	2.665	2.702	89.34	87.35	179.94	51
[PhTe(tu) ₂]Cl ^a	2.612	2.741	86.1	86.1	172.0	50
	2.616	2.766			172.37	53
[4-EtOC ₆ H ₄ Te(etu)·SC(NH)(morp)]Br	2.664	2.690	80.0	88.7	167.41	54
b. RTeLX Derivatives		Te-X		R-Te-X		
PhTe(tu)Cl	2.50	3.00			171.9	55
PhTe(tu)Br	2.50	3.11			179.1	55
PhTe(etu)Cl	2.521	2.849	89.22	87.29	176.03	56
PhTe(etu)Br C ₂ /c I ^b	2.556	2.835	89.05	86.46	175.96	57
PhTe(etu)Br P ₂ ₁ /c II ^b	2.523	2.969	89.45	87.02	177.22	57
PhTe(etu)I	2.614	3.003			175.88	58
PhTe(tmtu)Cl	2.595	2.668	88.40	87.49	175.41	2, 59
PhTe(tmtu)Br	2.589	2.833	88.98	88.59	177.0	2, 59
PhTe(trtu)Br	2.523	2.904			176.4	2

^a Long Te...Cl "bonds" (3.606 Å⁵⁰ or 3.578 Å⁵³) were detected in this compound. ^b Two different crystalline forms. In the crystalline form II weak Te...Br interactions (3.831 Å) associate the molecules in pairs.

**Figure 10.** T-shaped RTeS₂ and RTeSX complexes and interaction of the central tellurium atom with a fourth ligand.

pendicular to this direction, is occupied by an organic group. In the anion [PhTe(SCN)₂]⁻ there is no atom *trans* to the phenyl group and it has a clear T-shaped geometry. In [PhTe(tu)₂]Cl the T-shaped cation has a chlorine atom *trans* to the phenyl at a long distance.^{50,51} The relationship with square planar complexes is demonstrated by this long Te...Cl distance 3.606⁵⁰ or 3.578 Å.⁵³ still observed in the complex [PhTe(tu)₂]⁺Cl⁻, connecting the tellurium atom to the anionic chlorine, which can be regarded as a secondary bond.⁵⁰ The chloride ligand can be seen as the "missing" ligand from the fourth position of a square planar unit. It is located in a direction making an angle of 163° with the direction of the Te-C bond.⁵¹ The structure is explained by the strong *trans* influence of the phenyl group, which in fact expels the ligand (chlorine) situated *trans* to itself.⁵² Thus, the structure can be regarded as intermediate between square planar and true three-coordinate T-shaped complexes.⁵⁰⁻⁵⁴

Similar, but authentic T-shaped structures are observed in RTeLX compounds (L = monodentate sulfur ligand, X = halogen).⁵⁵⁻⁵⁹ Apparently, most of these are monomeric, with no Te...X interactions although in a few such derivatives very weak Te...X interactions *trans* to the phenyl group are observed. In this connection an interesting case is offered by the com-

**Figure 11.** Molecules of PhTe(etu)Br associated in dimers through weak Te...Br interactions.

pound PhTe(etu)Br, which exists in two crystalline forms.⁵⁷ The yellow form I is monoclinic (C₂/c) and contains T-shaped discrete PhTe(etu)Br molecules. The red form II is also monoclinic (P₂₁/c) but contains secondary Te...Br interactions (3.831 Å) making an angle of 162.2° with the Te-C_{Ph} bond, connecting the molecules in pairs (supramolecular Te...X dimers) as depicted in Figure 11.

The molecular dimensions of the compounds described in this section are listed in Table 9.

d. Two-Coordinate, Angular Complexes with a TeS₂ Unit

Some tellurium(II) complexes contain only two directly attached sulfur ligands with no other intermolecular interactions between the central atom of a molecule and the coordinated groups of another molecule. The resulting geometry may be regarded as a tetrahedron, from which two adjacent vertices are missing (occupied by two stereochemically active lone pairs). This is the case in the thiosulfato complexes [NH₄]₂[Te(SSO₃)₂],⁶⁰ Rb₂[Te(SSO₃)₂],⁶¹ Ba[Te(SSO₃)₂]ⁿH₂O (n = 2, 3)^{62,63} as well as the methane-, benzene-, and toluenethiosulfonatos Te(SSO₂R)₂ (R = Me, Ph, 4-MeC₆H₄).⁶⁴⁻⁶⁷ Their structures (Figure 12) are rather simple, and the molecular dimensions are listed in Table 10. In this case the tellurium-sulfur bonds are true 2c-2e normal covalent bonds and are among the shortest

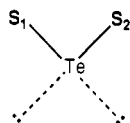


Figure 12. The TeS_2 units in $[\text{Te}(\text{SSO}_3)_2]_2^-$ and $\text{Te}(\text{SSO}_2\text{R})_2$ ($\text{R} = \text{Me}, \text{Ph}$) showing the two stereochemically active lone electron pairs.

Table 10. Molecular Dimensions in Two-Coordinate $[\text{Te}^{\text{IV}}\text{L}_2]$ Complexes

compound	bond lengths, Å Te–S	bond angles, deg $\text{S}_1\text{–Te–S}_2$	ref
$[\text{NH}_4]_2[\text{Te}(\text{SSO}_3)_2]$	2.36	103	60
$\text{Rb}_2[\text{Te}(\text{SSO}_3)_2]$	2.364, 2.370	100.1	61
$\text{Ba}[\text{Te}(\text{SSO}_3)_2] \cdot 2\text{H}_2\text{O}$	2.377	100.3	62
$\text{Ba}[\text{Te}(\text{SSO}_3)_2] \cdot 3\text{H}_2\text{O}$	2.384, 2.392	96.0	63
$\text{Te}(\text{SSO}_2\text{Me})_2$	2.36	100	64
$\text{Te}(\text{SSO}_2\text{Ph})_2$	2.380	97.61	65
	2.41	97	66
$\text{Te}(\text{SSO}_2\text{C}_6\text{H}_4\text{Me-4})_2$	2.41	96	67

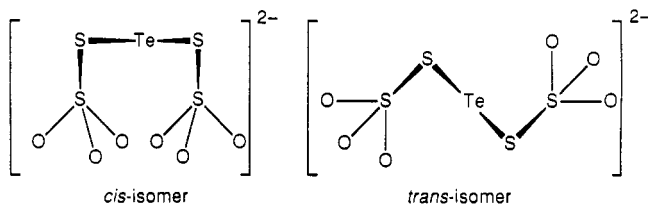


Figure 13. *Cis* and *trans* isomers of $[\text{Te}(\text{SSO}_3)_2]^{2-}$.

observed in tellurium–sulfur complexes. It is interesting to note that the bis(thiosulfato)tellurate(II) (“tellurapentathionato”) anions may adopt either *cis* or *trans* structures as found, for example in $\text{Ba}[\text{Te}(\text{SSO}_3)_2] \cdot 2\text{H}_2\text{O}$ and $\text{Ba}[\text{Te}(\text{SSO}_3)_2] \cdot 3\text{H}_2\text{O}$, respectively (Figure 13).

A closely related structure is that of $4\text{-EtOC}_6\text{H}_4\text{-TeSSO}_2\text{Me}(\text{SSO}_2\text{Me})_2$, which contains only one Te–S bond. In this compound, one of the two coordination sites is occupied by the aromatic group. The C–Te–S central site is angular (97.98°) with a short Te–S bond (2.40 Å).⁶⁸

C. Tellurium–Sulfur Complexes of Bidentate Ligands

1. Tellurium(IV) Complexes

a. Eight-Coordinate, Dodecahedral Complexes with TeS_8 Units

Most known eight-coordinate complexes known are dithiocarbamates^{69–76} and contain four equivalent bidentate ligands (Figure 14). The complexes are neutral molecular compounds in which the sulfur atoms occupy the corners of a (more or less) distorted D_{2h} dodecahedron (bisdisphenoid). The tellurium–sulfur bonds are not identical, but the differences are not dramatic (between 2.65 and 2.85 Å). Both Te–S bonds of a chelating ligand can be described as covalent, although they are longer than the sum of covalent radii. Perhaps the 3c–4e bonding scheme operates in these complexes as well, although it is less obvious which tellurium orbitals are involved in bonding. The ligand bite was found in the range around 2.94 Å, and interligand rather short S...S contacts of the order of 3.2 Å are observed.^{69,70} The molecular dimensions of the six complexes whose

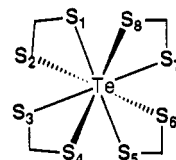


Figure 14. The tellurium environment in eight-coordinate, dodecahedral complexes with TeS_8 units and four bidentate ligands.

structures have been determined are given in Table 11. No secondary interactions are observed in any of these complexes.

In the compound $\text{Te}(\text{S}_2\text{CNET}_2)_3(\text{ClO}_4)$ only six sulfur atoms are present and the seventh and eighth coordination sites are occupied by the oxygens of a perchlorato group.⁷⁶ Thus, this anion should be incorporated in the coordination sphere, and the complex is correctly formulated as $[\text{Te}(\text{S}_2\text{CNET}_2)_3(\text{ClO}_4)]$.

b. Seven-Coordinate, Pentagonal Bipyramidal Complexes with TeS_7 Units

Seven-coordinate, pentagonal bipyramidal geometry can be achieved by combining three bidentate chelating ligands with an additional monodentate sulfur ligand such as a thiocyanato group. Two such complexes of this type have been investigated so far,^{77,78} and they present similar features. The chelating ligands occupy five equatorial positions and an axial one, whereas the monodentate sulfur-containing ligand is in the remaining axial position (Figure 15).

In $\text{Te}[(\text{S}_2\text{CN}(\text{Me})\text{CH}_2\text{CH}_2\text{OH})_3(\text{SCN})]$ the tellurium–sulfur interatomic distances are in the range from 2.52 to 2.88 Å. The lower values are only ~ 0.1 Å longer than the covalent bond lengths, but the longer values approach secondary bonding distances. The longest is the axial Te–S bond formed by the SCN ligand below the equatorial plane, and the shortest is also an axial Te–S bond, *trans* to SCN and coordinated to a bidentate chelating ligand. The axial $\text{S}_{\text{chel}}\text{–Te–S}_{\text{SCN}}$ sequence forms an angle of 168.5° .⁷⁸ The bond angles, shown together with the bond lengths in Table 12, show the effect of the small bite of the bidentate ligand, which makes the value of the $\text{S}_{\text{ax}}\text{–Te–S}_{\text{eq}}$ bond angle smaller than the theoretical value of 90° . In the equatorial plane, the small bite of the ligand in fact favors the pentagonal arrangement of the five sulfur atoms (required value 72°). It should also be noted that the axial Te–SCN bond (2.964 Å) is significantly longer than the sum of the covalent radii, owing to the *trans* influence of the chelating ligand, which seems to be bonded more firmly to tellurium than the SCN anion.

A second known example⁷⁷ is a related compound $\text{Te}[\text{S}_2\text{CN}(\text{CH}_2\text{CH}_2\text{OH})_2]_3(\text{SCN})$, which shows similar features, as illustrated by the molecular dimensions given in Table 12.

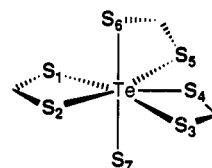


Figure 15. The TeS_7 pentagonal bipyramid in seven-coordinate $(\text{S–S})_3\text{TeS}$ derivatives.

Table 11. Molecular Dimensions of Eight-Coordinate, D_{2d} Dodecahedral (Bisdisphenoidal) TeS_8 Complexes

compound	bond lengths, Å		bond angles, deg			ref(s)
	short Te-S	long Te-S	intraligand S-Te-S	adjacent S-Te-S	trans S-Te-S	
$\text{Te}(\text{S}_2\text{CNET}_2)_4$ (I) ^a	2.669	2.732	65.6	69.3	159.8	69, 70
	2.644	2.740	66.1	70.8	159.6	
	2.774	2.819	63.1			
	2.782	2.797	63.6			
$\text{Te}(\text{S}_2\text{CNET}_2)_4$ (II) ^a	2.631	2.689	66.5	70.0	158.7	70
	2.651	2.774	65.3	69.7	160.9	
	2.821	2.845	63.2			
	2.763	2.771	64.4			
$\text{Te}(\text{S}_2\text{CNPr}_2)_4$	2.704	2.735	64.9	not given		71
	2.727	2.804	63.7			
	2.698	2.709	65.4			
	2.646	2.812	64.5			
$\text{Te}[\text{S}_2\text{CN}(\text{Me})\text{C}_2\text{H}_4\text{OH}]_4$	2.714	2.758	65.11	69.90	160.00	72
$\text{Te}[\text{S}_2\text{CN}(\text{C}_2\text{H}_4\text{OH})_2]_4$	2.707	2.857	63.8	73.6	155.4	73
	2.712	2.736	65.5	75.4	155.5	
	2.637	2.824	65.5			
	2.712	2.716	65.7			
$\text{Te}[\text{S}_2\text{C}(\text{morph})]_4$	2.694	2.824	64.40	75.78	155.21	74, 75
	2.684	2.752	65.34	73.82	155.75	
	2.672	2.824	64.56			
	2.702	2.744	65.16			
$\text{Te}(\text{S}_2\text{CNET}_2)_3(\text{ClO}_4)^b$	2.426	2.790	68.8	not given		76
	2.590	2.732	66.8			
	2.598	2.753	67.2			

^a Two independent molecules in the unit cell. ^b Two oxygen atoms of ClO_4 occupy two corners of the dodecahedron replacing a dithiocarbamate group; $\text{Te}\cdots\text{O}$ distances 3.124 and 2.876 Å.

Table 12. Molecular Dimensions in Seven-Coordinate, Pentagonal Bipyramidal $[\text{Te}(\text{S}-\text{S})_3\text{L}]$ Derivatives

compound	bond lengths, Å		bond angles, deg			ref
	chelate Te-S	monodentate Te-S	intraligand S-Te-S	interligand S-Te-S	transaxial $\text{S}_6\text{-Te-S}_7$	
$\text{Te}[\text{S}_2\text{CN}(\text{C}_2\text{H}_4\text{OH})_2]_3\text{SCN}$	Te-S ₁ 2.724	Te-S ₇ 2.964	66.7	76.5	169.8	77
	Te-S ₂ 2.649		67.0	76.3		
	Te-S ₃ 2.629		68.5	76.7		
	Te-S ₅ 2.781					
	Te-S ₆ 2.460					
$\text{Te}[\text{S}_2\text{CN}(\text{Me})\text{C}_2\text{H}_4\text{OH}]_3\text{SCN}$	Te-S ₁ 2.72	Te-S ₇ 2.88	65.8	71.5	168.5	78
	Te-S ₂ 2.60		68.0	77.2		
	Te-S ₃ 2.64		67.9	77.3		
	Te-S ₄ 2.72					
	Te-S ₅ 2.79					
	Te-S ₆ 2.52					

c. Seven-Coordinate, Pentagonal Bipyramidal Complexes with TeS_6X and TeS_6R Units

Several tris(dithiocarbamato) complexes bearing an additional halogen coordinated to tellurium(IV) of the type $\text{Te}(\text{dte})_3\text{X}$, and monoorganotellurium(IV) tris(dithiocarbamato) complexes of the type $\text{RTe}(\text{dte})_3$, exhibit pentagonal bipyramidal geometries, with the halogen atom or the organic group in an axial position, conventionally depicted below the pentagonal plane (Figure 16). The known examples⁷⁹⁻⁸⁵ are listed in Table 13. As in previous examples, the axial Te-S bond (to the sulfur above the equatorial plane), *trans* to the halogen atom, is the shortest. In the phenyltellurium derivative $\text{PhTe}(\text{S}_2\text{CNET}_2)_3$ the phenyl group occupies an axial position under the equatorial plane,^{69,83} but the axial Te-S bond is the longest Te-S bond in the coordination sphere suggesting that the *trans* influence of the phenyl group is much stronger than that of a halogen. The axial bonds form a C-Te-S bond angle of only 144.6°, instead of 180°, which indicates strong distortions from the ideal geometry.⁸³ The same is observed in *p*-MeOC₆H₄Te(S₂CNMe₂)₃,⁸⁵ with an angle

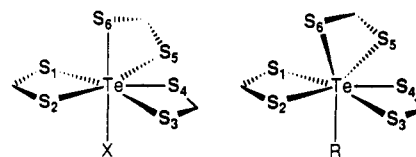


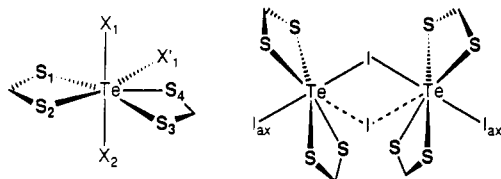
Figure 16. Tellurium environments in pentagonal bipyramidal complexes of the types $\text{Te}(\text{dte})_3\text{X}$ and $\text{RTe}(\text{dte})_3$.

of 143.7° between the axial Te-C and Te-S bonds. The distortions of the structures can be explained in terms of a ψ -dodecahedral geometry, with an active lone electron pair occupying the vacant vertex of the dodecahedron.⁸⁵

In the mixed-ligand complex $\text{PhTe}(\text{S}_2\text{CNET}_2)_2[\text{S}_2\text{P}(\text{OEt})_2]$ the dithiophosphato ligand supplies the sulfur atom in the axial position with the weak Te-S bond *trans* to the phenyl group and a single sulfur atom in the equatorial plane.⁸⁴ The C-Te-S bond angle of 148° illustrates the geometry deformation. The sulfur atoms of the dithiocarbamato ligands occupy four equatorial positions. The fifth equatorial position is occupied by a sulfur atom of the dithiophosphate ligand.⁸⁴

Table 13. Molecular Dimensions of Seven-Coordinate, Pentagonal Bipyramidal [Te^{IV}(S-S)₃X] and [RTe^{IV}(S-S)₃] Complexes

compound	bond lengths, Å			ref(s)
	Te-S		Te-X(R)	
a. Halogeno Derivatives				
Te(S ₂ CNEt ₂) ₃ Cl·dioxane	2.675, 2.594, 2.605, 2.773, 2.874, 2.522(ax)		2.686(Cl)	79
Te[S ₂ CN(C ₂ H ₄ OH) ₂] ₃ Cl·2H ₂ O	2.729, 2.640, 2.623, 2.689, 2.800, 2.464 (ax)		2.813(Cl)	80
Te[S ₂ CN(Me)(C ₂ H ₄ OH) ₂] ₃ Cl·2H ₂ O	2.755, 2.593, 2.587, 2.731, 2.835, 2.493(ax)		2.772(Cl)	81
Te[S ₂ CN(Me)C ₂ H ₄ OH] ₃ Br	2.71 (eq), 2.51 (ax)		2.83(Br)	72
Te(S ₂ CNC ₆ H ₁₀) ₃ I	2.555 (ax), 2.707, 2.722, 2.673, 2.713, 2.671		3.036(I)	82
b. Aryl Derivatives				
PhTe(S ₂ CNEt ₂) ₃	2.701, 2.797, 2.816, 2.657, 2.606, 3.228(ax)		2.124(Ph)	69, 83
PhTe(S ₂ CNEt ₂) ₂ [S ₂ P(OEt) ₂]	2.696, 2.690, 2.708, 2.674, 2.700		3.436 (ax Te...S)	84
4-MeOC ₆ H ₄ Te(S ₂ CNMe ₂) ₃	2.591, 2.792, 2.646, 2.868, 2.706		3.277 (ax Te...S)	85

**Figure 17.** (Left) The tellurium coordination in Te[S₂CN(CH₂CH₂OH)₂]₂I₂ and (right) the tellurium coordination in the dimer unit [Te(S₂CN(CH₂CH₂OH)₂]₂I₂].

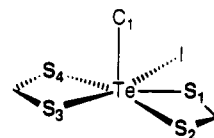
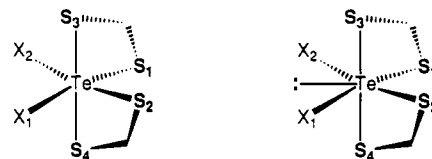
The data reveal a remarkable difference between halogenotriss(dithiocarbamato)tellurium(IV) complexes and aryltellurium(IV) tris(dithiocarbamate) complexes in terms of the properties of the axial bonds in accord with the difference in the bonding character of Te-C and Te-halogen bonds (*trans* influence). It should also be noted that in Te(dtc)₃X the equatorial sulfur of the S_{ax}-S_{eq} ligand is well above the equatorial plane, while it is *in* the equatorial plane in RTe(dtc)₃ (Figure 16).

d. Seven-Coordinate, Pentagonal Bipyramidal Complexes with TeS₄X₃ and TeS₄X₂R Units

Pentagonal bipyramidal geometry is also observed in the complex Te[S₂CN(CH₂CH₂OH)₂]₂I₂,⁸⁶ which displays some interesting features. Thus while four equatorial Te-S bonds exhibit bond lengths in the range expected for this type of compound (short 2.52 Å and long 2.76 Å), the tellurium-iodine bonds are very different: an axial short Te-I bond (2.842 Å) below the equatorial plane, an axial long Te-I bond (3.044 Å) above the equatorial plane, and a secondary bond to an equatorial iodine atom Te...I (3.427 Å), which belongs to a second molecule. Thus, the pentagonal bipyramidal unit is connected to a similar second one, and the compound is in fact a doubly bridged dimer, as shown schematically in Figure 17. The *trans* X₁-Te-X₂ (X = I) angle is 173.8° and the Te-I bonds are quasiperpendicular to the distorted equatorial plane as shown by the I-Te-S bond angles (e.g., 89.6°, 92.7°, 85.0°, and 92.1° for X₁ and 88.7°, 92.2°, 93.1°, and 92.6° for X₂). The non-*trans* X-Te...X' angles are 88.3° and 85.4°. In the equatorial plane the intraligand (biting) S-Te-S angles are 76.5° and 67.0°, whereas the S₁-Te...I', S₃-Te...I', and S₂-Te-S₄ angles of 74.0°, 72.5°, and 78.9°, respectively, are close to values expected in a (distorted) pentagon.⁸⁶

e. Six-Coordinate, Pentagonal Pyramidal Complexes with TeS₄XR Units

The complex Te(S₂CNEt₂)₂(CH₃)I exhibits a pentagonal pyramidal geometry (Figure 18) with the methyl

**Figure 18.** The tellurium coordination in Te(S₂CNEt₂)₂(CH₃)I.**Figure 19.** The tellurium environment of TeS₄X₂ complexes (e.g., Te(S₂CNPrⁱ)₂I₂), interpreted as a distorted octahedron or trapezoidal bipyramid (left) or as a ψ-pentagonal bipyramid (right).

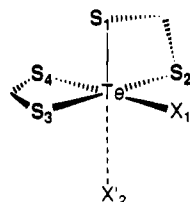
group in the axial position and four sulfur atoms and an iodine atom in equatorial positions.⁸⁴ This geometry can also be described as ψ-pentagonal bipyramidal, with a stereochemically active axial lone pair. The dithiocarbamate ligands are unsymmetrically chelated (Te-S bond lengths 2.725, 2.646, 2.691, and 2.618 Å and Te-I 3.1165 Å) and the structure is relatively strain-free. The axial-equatorial bond angles are near 90° (C-Te-I 85.38°, C-Te-S₁ 86.43°, C-Te-S₂ 87.95°, C-Te-S₃ 89.34°, and C-Te-S₄ 88.53°). In the equatorial plane the bond angles within the chelate rings are small as usual (S₁-Te-S₂ 66.25°, S₃-Te-S₄ 67.13°) with closer to expected values (72°) for the interligand bond angles (S₂-Te-S₃ 74.64°, S₁-Te-I 76.11°, and S₄-Te-I 75.46°).⁸⁴

f. Six-Coordinate Distorted Octahedral Complexes with TeS₄X₂ Units

The geometry of TeS₄X₂ complexes, illustrated by Te(S₂CNPrⁱ)₂I₂, is described as distorted octahedral (Figure 19).⁸⁷ The two halogen (iodine) atoms are in *cis* positions and form a rather broad I-Te-I angle of 105°, suggesting the possible presence of a stereochemically active lone pair of electrons within this angle but there is also an S-Te-I angle of 117° where the lone pair could be located. These complexes represent the transition between octahedral and pentagonal bipyramidal complexes. If the lone pair is taken into consideration, the complex can be described as ψ-pentagonal bipyramidal. It is not quite clear whether the observed geometry, with small S-Te-S bond angles (70.1° and 69.0°) close to the 72° angles of a regular pentagon, is due to a ψ-pentagonal bipyramidal geom-

Table 14. Molecular Dimensions of Six-Coordinate Distorted $[\text{Te}^{\text{IV}}(\text{S}-\text{S})_2\text{X}_2]$ Octahedral Complexes

compound	bond distances, Å	bond angles, deg	ref
<i>cis</i> - $\text{Te}(\text{S}_2\text{CNPr}^i)_2\text{I}_2$	Te-S ₁ 2.532	I ₁ -Te-I ₂ 104.8	87
	Te-S ₂ 2.593	I ₂ -Te-S ₁ 89.4	
	Te-S ₃ 2.567	I ₁ -Te-S ₂ 89.6	
	Te-S ₄ 2.590	S ₁ -Te-S ₂ 87.5	
	Te-I ₁ 3.046	S ₁ -Te-I ₁ 149.1	
	Te-I ₂ 2.976	S ₂ -Te-I ₂ 156.2	
		S ₃ -Te-S ₁ 70.1	
		S ₂ -Te-S ₄ 69.0	
		S ₁ -Te-S ₄ 90.1	
		S ₃ -Te-S ₂ 101.8	
		I ₁ -Te-S ₄ 117.3	
		I ₂ -Te-S ₃ 99.3	
		S ₃ -Te-I ₁ 80.5	
		S ₄ -Te-I ₂ 87.3	
<i>cis</i> - $\text{Te}(\text{S}_2\text{CNEt}_2)_2\text{Br}_2$	Te-S ₁ 2.566	S ₂ -Te-S ₁ 71.1	88
	Te-S ₂ 2.555	Br ₁ -Te-S ₁ 165.2	
	Te-S ₃ 2.666	Br ₂ -Te-S ₂ 153.1	
	Te-S ₄ 2.524	S ₂ -Te-S ₄ 69.0	
		S ₂ -Te-S ₃ 89.6	
		S ₂ -Te-S ₄ 89.6	
		S ₂ -Te-S ₃ 89.6	

**Figure 20.** The tellurium environment in the cation $[\text{Te}(\text{S}_2\text{CNMe}_2)_2\text{Br}]^+$.

etry caused by the presence of a lone electron pair or is the result of the small bite of the chelating ligand. Therefore, the stereochemical activity of the lone pairs must be interpreted with some caution. Strong distortions owing to the small bites of the ligand are observed in the *trans* axial bonds, which form angles of 149.1° and 156.2°, which are much smaller than those required for colinear bonds. The tellurium-sulfur bond lengths are in the range of 2*c*-2*e* normal covalent bonds.⁸⁷ Other molecular dimensions are listed in Table 14.

A related structure is that of *cis*- $\text{Te}(\text{S}_2\text{CNEt}_2)_2\text{Br}_2$.⁸⁸ The Te-S bond distances are almost equal, thus making the ligand almost isobidentate (2.566–2.666 Å), but the interhalogen bond angle (94.8°) has an almost normal value, close to 90°. The *trans* atoms form bond angles Br-Te-S of 165.2° and 153.1°, showing again distortions from the octahedral geometry. Other data are listed in Table 14.

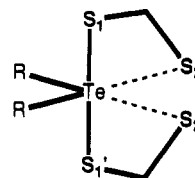
In the cation $[\text{Te}(\text{S}_2\text{CNMe}_2)_2\text{Br}]^+$ the ligands form a square pyramid, but the secondary Te...Br bond to the accompanying anion, $[\text{Te}(\text{S}_2\text{CNMe}_2)\text{Br}]^-$, completes the coordination to distorted octahedral⁸⁹ (Figure 20). Other molecular dimensions are listed in Table 15.

g. Six-Coordinate, Distorted Octahedral Complexes with TeS_4R_2 Units

Bidentate ligands in diorganotellurium derivatives strongly distort the octahedral coordination. This type of structure is illustrated by $\text{Me}_2\text{Te}(\text{S}_2\text{CNMe}_2)_2$ ⁹⁰ and $\text{Ph}_2\text{Te}(\text{S}_2\text{CNMe}_2)_2$ (Figure 21).⁹¹ Two sulfur atoms occupy axial positions, but intramolecular secondary bonds between tellurium and the second sulfur of each ligand are formed. The secondary bonded sulfur atoms

Table 15. Molecular Dimensions of the Cation $[\text{Te}(\text{S}_2\text{CNMe}_2)_2\text{Br}]^+$

compound	bond distances, Å	bond angles, deg	ref
$[\text{Te}(\text{S}_2\text{CNMe}_2)_2\text{Br}]^+$	Te-S ₁ 2.445	in the equatorial plane:	89
	Te-S ₂ 2.594	S ₃ -Te-S ₄ 70.1	
	Te-S ₃ 2.620	S ₂ -Te-S ₄ 89.0	
	Te-S ₄ 2.571	S ₂ -Te-Br ₁ 103.9	
	Te-Br ₁ 2.725	transaxial bonds:	
	Te...Br ₂ 3.307	S ₂ -Te-S ₃ 145.6	
		Br ₁ -Te-S ₄ 162.6	
		axial-equatorial angles:	
		S ₁ -Te-Br ₁ 86.6	
		S ₁ -Te-S ₂ 71.1	
		S ₁ -Te-S ₄ 86.7	
		S ₁ -Te-S ₃ 80.4	

**Figure 21.** The distorted octahedral tellurium coordination in TeS_4R_2 derivatives such as $\text{Ph}_2\text{Te}(\text{S}_2\text{CNMe}_2)_2$.

S_2 and S_2' are considerably above and below the (equatorial) C_1TeC_2 plane, as if being pulled by the axial sulfur atoms. This can be due to the small bite of the ligands, but it has been also interpreted as being caused by the tendency of these sulfur atoms to avoid the lone pair of electrons at tellurium.⁹¹ Similar structures were observed in other dithiocarbamates,⁹² in some diorganotellurium phosphorodithioates,^{93–95} a xanthate,⁹⁵ and in a mixed ligand compound.⁹⁵ Molecular dimensions for compounds belonging to this type are listed in Table 16.

The strong distortions of the coordination geometry observed in $\text{C}_6\text{H}_4(\text{CH}_2)_2\text{Te}(\text{S}_2\text{CNEt}_2)_2$ suggest that a satisfactory description of the tellurium coordination might be a ψ -trigonal bipyramid⁹⁶ in which a position in the equatorial plane is occupied by a stereochemically active lone pair. With short and long intraligand Te-S bond lengths (2.599 and 3.220 Å; 2.622 and 3.720 Å) and S-Te-S bond angles of 60.89° and 59.74° (in the chelate rings), 168.55° (transaxial), and 126.73° and 122.18° (interligand) the tellurium environment is very irregular (Table 16).

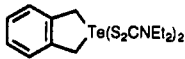
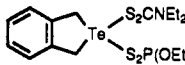
The structure of the mixed ligand complex $\text{C}_6\text{H}_4(\text{CH}_2)_2\text{Te}(\text{S}_2\text{CNEt}_2)_2[\text{S}_2\text{P}(\text{OEt})_2]^{95}$ deserves a comment. While the molecule exhibits the same geometrical features as the dithiocarbamates and dithiophosphates, there are significant differences between the Te-S bond lengths of the two ligands. Thus the Te-S bonds to the diethyldithiocarbamate ligand are shorter than those to the diethyl dithiophosphate ligand (see Table 16).

It is worth mentioning here that the xanthates appear to have a greater tendency to exhibit supramolecular association and some compounds of the general type $\text{R}_2\text{Te}(\text{S}_2\text{COR}')_2$ are discussed in section D.

h. Six-Coordinate, Distorted Octahedral Complexes with TeS_2X_4 Units

A complex of unusual composition, $\text{Te}_2\text{Br}_5(\text{S}_2\text{CNEt}_2)_3$, prepared from TeBr_4 and sodium dimethyldithiocarbamate was found by X-ray diffraction to be

Table 16. Molecular Dimensions of Six-Coordinate TeS₄R₂ Derivatives^a

compound	bond distance, Å		bond angle, deg: coaxial S ₁ -Te-S ₁ '	other	ref
	Te-S ₁ Te-S ₁ '	Te...S ₂ Te...S ₂ '			
Me ₂ Te(S ₂ CNMe ₂) ₂ ^b	2.654 2.621	3.173 3.167	167.58	S ₁ -Te-C: 89.2°, 83.4° S ₁ -Te-S ₂ : 61.0°	90
Me ₂ Te(S ₂ CNMe ₂) ₂ ^b	2.629 2.605	3.244 3.182	165.39	S ₁ -Te-C: 88.2°, 82.1° S ₁ -Te-S ₂ : 60.1°	90
Ph ₂ Te(S ₂ CNMe ₂) ₂	2.621	3.186	172.0	S ₁ -Te-C ₂ : 91.5°, 83.3° S ₁ -Te-S ₂ : 61.0°	91
Ph ₂ Te(S ₂ CNEt ₂) ₂	2.615 2.630	3.130	179.0 175.11	S ₁ -Te-S ₂ : 61.84	92
Ph ₂ Te(S ₂ CNEtPh) ₂	2.618	3.184	171.2		92
Ph ₂ Te(S ₂ CNBu ₂) ₂	2.622	3.195	173.2	S ₁ -Te-C: 89.5°, 85.7° S ₁ -Te-S ₂ : 60.1°	
Ph ₂ Te(S ₂ CNPh ₂) ₂	2.608	3.204	172.5		92
(4-MeOC ₆ H ₄) ₂ Te(S ₂ CNMe ₂) ₂	2.628 2.609	3.258 3.183	177.8	S ₁ -Te-C: 92.7°, 86.3°	90
Ph ₂ Te[S ₂ P(OMe) ₂] ₂	2.619 2.625	3.383 3.362	171.8	S ₁ -Te-C: 89.4° S ₁ -Te-S ₂ : 66.9°	93
Ph ₂ Te[S ₂ P(OEt) ₂] ₂	2.609 2.620	3.367 3.353	170.6	S ₁ -Te-S ₂ : 66.58°	94
 Te(S ₂ CNEt ₂) ₂	2.599 2.622	3.220 3.270	168.55	S ₁ -Te-C: 90.9°, 82.9° S ₁ -Te-S ₂ : 60.89°	96
 Te(S ₂ CNEt ₂) ₂ S ₂ P(OEt) ₂	2.521(dtc) 2.742(dtp)	3.103(dtc) 3.438(dtp)	171.75	S ₁ -Te-S ₂ : 63.54° (dte) S ₁ -Te-S ₂ : 64.60 (dtp) S ₂ -Te-S ₂ ': 123.06 (dtp/dtc)	95

^a Some compounds related to these exhibit supramolecular associations and are discussed in Section D. ^b Two independent molecules are present in the unit cell.

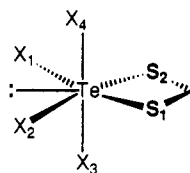


Figure 22. The distorted octahedral or ψ -pentagonal bipyramidal tellurium coordination in the anion [Te(S₂CNEt₂)Br₄]⁻.

Table 17. Molecular Dimensions in the Anion Present in Te₂Br₅(S₂CNMe₂)₃

anion	bond lengths, Å	bond angles, deg	ref
[Te(S ₂ CN- Et ₂)Br ₄] ⁻	Te-S ₁ 2.531 Te-S ₂ 2.481 Te-Br ₁ 2.911 Te-Br ₂ 2.813 Te-Br ₃ 2.686 Te-Br ₄ 2.689	in the equatorial plane: S ₁ -Te-S ₂ 71.5° Br ₁ -Te-S ₁ 79.1° Br ₂ -Te-S ₂ 78.3° Br ₁ -Te-Br ₂ 131.0° coaxial bond: Br ₃ -Te-Br ₄ 175.3° axial-equatorial bonds: Br ₂ -Te-Br ₄ 90.4° Br ₃ -Te-Br ₁ 85.3° Br ₂ -Te-Br ₄ 91.6° Br ₃ -Te-Br ₂ 92.8° Br ₃ -Te-S ₂ 93.8° Br ₃ -Te-S ₁ 90.3°	89

an ionic compound,⁸⁹ in which both the anion and the cation contain tellurium(IV), but in very different coordination environments; the compound can be best written as [Te(S₂CNEt₂)₂Br]⁺[Te(S₂CNEt₂)Br₄]⁻. The anion is a very distorted octahedron, or a ψ -pentagonal bipyramid, as discussed in the previous section (Figure 22), whereas the cation displays ψ -octahedral geometry. The molecular dimensions, given in Table 17, show a Br-Te-Br axial segment (175.3° bond angle) perpendicular to the plane formed by Br₁S₁S₂Br₄. The small angles in the equatorial plane within the chelate ring (S-Te-S 71.5°) and between the sulfur atom and the bromines (S-Te-Br 79.1° and 78.3°) combined with a large Br-Te-Br angle in the equatorial plane (131.0°) suggest that a fifth position of a pentagon is occupied

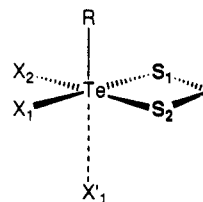


Figure 23. The distorted octahedral tellurium coordination in *p*-MeOC₆H₄Te[S₂P(OMe)₂]Br₂.

Table 18. Molecular Dimensions of *p*-MeOC₆H₄Te[S₂P(OMe)₂]Br₂

compound	bond lengths, Å	bond angles, deg	ref
<i>p</i> -MeOC ₆ H ₄ Te[S ₂ P- (OMe) ₂]Br ₂	Te-S ₁ 2.632 Te-S ₂ 2.728 Te-C 2.127 Te-Br ₁ 2.677 Te-Br ₂ 2.616 Te...Br ₁ ' 3.810	in equatorial plane: S ₁ -Te-S ₂ 75.8° Br ₂ -Te-S ₁ 92.8° Br ₁ -Te-S ₂ 98.2° Br ₁ -Te-Br ₂ 92.3° axial-equatorial bonds C-Te-S ₁ 89.9° C-Te-S ₂ 88.0°	93

by a stereochemically active lone pair.

i. Six-Coordinate, Distorted Octahedral Complexes with TeS₂X₂R Units

This coordination type is found in an organotellurium(IV) dialkylphosphorodithioate, *p*-MeOC₆H₄Te{S₂P(OMe)₂}Br₂,⁹³ a molecular compound in which the ligands form a tetragonal pyramid. However, if the intermolecular Te...Br secondary interactions (3.810 Å) are considered, the coordination geometry becomes distorted octahedral (Figure 23). The molecular dimensions are listed in Table 18. As usual, the S-Te-S bond angle determined by the ligand bite is small (75.8°) but the unstrained bond angles in the equatorial plane (S-Te-Br and Br-Te-Br) are close to normal.

Table 19. Molecular Dimensions of Five-Coordinate, Trigonal Bipyramidal $[R_2Te^{IV}(S-S)X]$ Complexes

compound	bond lengths, Å			bond angles, deg				ref
	Te-S ₁	Te-S ₂	Te-X	chelate S ₁ -Te-S ₂	coaxial X-Te-S ₁	ax-eq R-Te-S ₁	R-Te-R	
Ph ₂ Te(S ₂ CNEt ₂)Cl			X = Cl					94
molecule I ^a	2.516	3.112	2.638	62.5	172.0	92.3, 84.1	98.2	
molecule II ^a	2.513	3.184	2.616	61.8	168.7	92.4, 83.2	98.5	
Ph ₂ Te(S ₂ CNPr ₂)Cl	2.484	3.149	2.661	62.0	173.2	85.7, 92.2	96.0	94
Ph ₂ Te(S ₂ CNEt ₂)Br			X = Br					98
molecule I ^a	2.518	3.183	2.743	62.2	169.2	84.2, 92.2	98.7	
molecule II ^a	2.516	3.113	2.779	62.5	172.9	84.4, 92.4	98.1	

^a Two independent molecules in the unit cell.

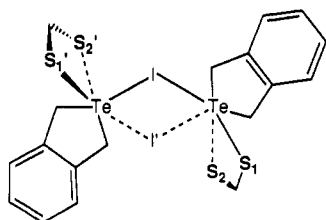


Figure 24. The iodine-bridged dimeric structure leading to a $TeS_2R_2X_2$ unit.

j. Six-Coordinate, Distorted Octahedral Complexes with $TeS_2X_2R_2$ Units

The benzotellurole derivative $C_6H_4(CH_2)_2Te(S_2CNEt_2)I$ dimerizes through a pair of iodine bridges and each tellurium atom in the resulting compound is surrounded by two carbon, two sulfur, and two iodine atoms (Figure 24).⁹⁷

If the coordination geometry is described as octahedral, it should be regarded as very distorted. Some bond angles have values close to perpendicular (e.g., I-Te-I' 92.35°, I-Te-C₈ 86.15°, C₈-Te-C₁ 85.3°, C₁-Te-S₁ 92.15°) but the S₁-Te-S₂ angle of the chelate ring is small as expected (63.83°) while the S₂-Te-I' bond angle (115.74°) suggests that a stereochemically active lone pair may occupy a position opposite to the $C_6H_4(CH_2)_2$ group. If the long Te...S₂ and Te...I' interactions are ignored a good ψ -trigonal bipyramidal geometry is obtained. The *trans*-axial bond angles (C₁-Te-I' 159.83° and C₈-Te-S₂ 146.14°) are smaller than 180°. Because of these distortions, the original paper⁹⁷ describes the geometry as ψ -pentagonal bipyramidal. The bond lengths are also unsymmetrical (Te-S₁ 2.490 Å, Te-S₂ 3.084 Å, Te-I 3.103 Å, and Te-I' 3.698 Å).

k. Five-Coordinate, Trigonal Bipyramidal Complexes with TeS_2XR_2 Units

Strongly distorted trigonal bipyramidal geometry is formed in complexes of the type $Ph_2Te(dtc)X$ (X = Cl, Br).^{94,98} The small bite of the ligand distorts the geometry and with S-Te-S bond angles of ~62° pulls down the S₂ atom from the equatorial plane (Figure 25). This is similar to what happens to Te-S_{eq} bonds

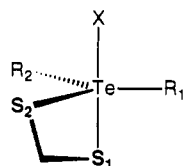


Figure 25. The trigonal bipyramidal tellurium environment in $Ph_2Te(dtc)Cl$ and other compounds with TeS_2XR_2 units.

in the S_{eq}-S_{ax} system of $Te(S-S)_3X$ complexes. The unstrained bond angles (R-Te-S) have close to normal values (Table 19).

l. Four-Coordinate, ψ -Trigonal Bipyramidal Complexes with TeS_2O_2 Units

Bis(monothioxyrocatecholato)tellurium(IV) exhibits a coordination geometry which can be described as ψ -trigonal bipyramidal (Figure 26). The two oxygen atoms occupy axial positions, but the *trans* axial angle is reduced to 160.3°, probably owing to the small bite of the ligands (and smaller than normal OTeS angles in the chelate rings).⁹⁹ Molecular dimensions are listed in Table 20.

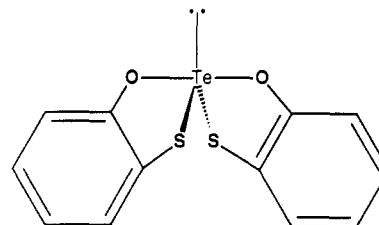
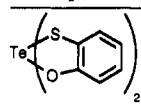


Figure 26. The tellurium environment in bis(monothioxyrocatecholato)tellurium(IV).

Table 20. Molecular Dimensions of Bis(monothioxyrocatecholato)tellurium(IV)

compound	bond lengths, Å		bond angles, deg	ref
	Te-S	Te-O		
	2.392	2.073	in the chelate rings:	99
	2.382	2.043	O ₂ -Te-S ₁ 81.8 O ₂ -Te-S ₂ 82.9 in the equatorial plane: S ₁ -Te-S ₂ 101.7 axial-equatorial angles: O ₁ -Te-S ₂ 84.7 O ₂ -Te-S ₁ 85.9	

Somewhat related to this type is the structure of X_2TeS_7 (X = Cl, Br) in which the two sulfur atoms in the equatorial positions are part of an eight-membered TeS_7 ring and the axial positions are occupied by halogens.¹⁰⁰ The S-Te-S angle in the eight-membered ring is large (100.15° for X = Cl; 99.49° for X = Br) which indicates little strain. The Te-S bonds are short (2.455 Å for X = Cl; 2.466 Å for X = Br).¹⁰⁰

2. Tellurium(II) Complexes

a. Five-Coordinate, Pentagonal Planar Complexes with TeS_5 and TeS_4X Units

Two types of pentagonal planar coordination environments have been found in tellurium(II) chemistry

Table 21. Five-Coordinate, Pentagonal Planar Complexes with TeS₅ and TeS₄N Units

compound	bond lengths, Å		bond angles, ^a deg	ref(s)
	short	long		
[Et ₄ N][Te(S ₂ COEt) ₃] ^b	Te-S ₁ 2.679 Te-S ₄ 2.647 Te-S ₅ 2.497	Te-S ₂ 3.059 Te-S ₃ 3.051	S ₁ -Te-S ₂ 82.1 S ₁ -Te-S ₃ 61.7 S ₂ -Te-S ₃ 73.6 S ₃ -Te-S ₄ 62.1 S ₄ -Te-S ₅ 80.8	101, 102
Te ₂ (μ-4,4'-bipy)(S ₂ COEt) ₄	Te-S ₂ 2.548 Te-S ₃ 2.539	Te-S ₁ 2.814 Te-S ₄ 2.839 Te-N 2.892	S ₁ -Te-S ₂ 65.98 S ₂ -Te-S ₃ 78.56 S ₃ -Te-S ₄ 65.95 S ₄ -Te-N 77.6 N-Te-S ₁ 72.2	103

^a Note the smaller angles within the chelate rings. ^b One xanthato ligand (S₅) is monodentate.

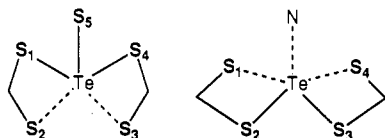


Figure 27. Planar pentagonal coordination of tellurium with sulfur ligands.

(Figure 27). Thus, in the [Te(S₂COEt)₃]⁻ anion, two xanthato ligands are bidentate chelating (unsymmetrical or anisobidentate) whereas the third xanthato ligand is monodentate. A planar pentagonal geometry results from this arrangement.^{101,102} In a binuclear 4,4'-bipyridyl complex of the type Te₂(μ-4,4'-bipy)(S₂COEt)₄ two ethylxanthato ligands are bidentate chelating, and a fifth position in the pentagon is occupied by the nitrogen atom of 4,4'-bipyridyl.¹⁰³ Each of the two nitrogen atoms participates in such coordination and the compound should be written as (EtOCS₂)₂Te(μ-4,4'-bipy)Te(S₂COEt)₂. The molecular dimensions are listed in Table 21. In both compounds short and long Te-S bonds are observed with significant differences in the interatomic distances suggesting a pair of bonds to be secondary interactions (Figure 27).

b. Four-Coordinate, Trapezoidal and Square Planar Complexes With TeS₄ Units

1,1-Dithiolates, e.g., dithiocarbamates and xanthates, form a series of tellurium(II) complexes acting as bidentate chelating ligands. The small bite of the ligands (~2.95 Å) imposes certain restraints upon the coordination geometry and usually results in the deformation of the square so that the geometry around tellurium becomes trapezoidal (Figure 28). Obviously, the distortion from regular square planar observed for monodentate sulfur ligands in complexes with TeS₄ units (as discussed above) is caused by the small bite of the ligands. A typical example is that of tellurium(II) diisopropyl xanthate, Te(S₂COPrⁱ)₂.¹⁰⁴ This contains short and long Te-S bonds (Table 22). Within the chelate rings the S-Te-S bond angles are considerably smaller than 90°. One of the interligand bond angles, namely S(2)-Te-S(4), is very large (~145°). Thus a distorted quadrangle (trapezoid) can be interpreted as a pentagon with a missing corner. Methyl- and ethylxanthate complexes exhibit similar geometries, but they display supramolecular association (see below). Bulky isopropyl groups apparently prevent intermolecular contacts and the complex remains monomeric. Molecular dimensions are listed in Table 22.

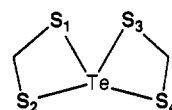


Figure 28. Trapezoidal TeS₂ geometry in Te(S₂COPrⁱ)₂ and related compounds.

Table 22. Molecular Dimensions of Trapezoidal Te(S-S)₂ Complexes

compound	bond lengths, Å		bond angles, deg	ref
	short Te-S	long Te-S		
Te(S ₂ COPr ⁱ) ₂	Te-S ₁ 2.483 Te-S ₃ 2.497	Te-S ₂ 2.877 Te-S ₄ 2.881	S ₁ -Te-S ₂ 65.9 S ₃ -Te-S ₄ 65.9 S ₁ -Te-S ₃ 83.7 S ₂ -Te-S ₄ 144.1	104
[Ph ₄ As] ₂ [Te{S ₂ C=C(CN) ₂ }] ₂	Te-S ₁ 2.524 Te-S ₃ 2.463	Te-S ₂ 2.945 Te-S ₄ 2.819	S ₁ -Te-S ₂ 65.0 S ₃ -Te-S ₄ 67.3 S ₁ -Te-S ₃ 79.6 S ₂ -Te-S ₄ 148.0	105

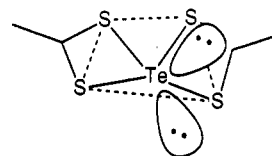
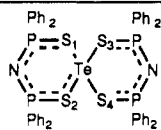
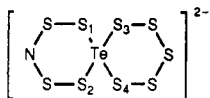


Figure 29. Suggested location of the two lone pairs in trapezoidal Te^{II}S₄ complexes.

The structure of [Ph₄As]₂[Te{S₂C=C(CN)₂}]₂ is remarkably similar¹⁰⁵ in spite of the different chemical nature of the ligand. This anion is one of the few examples of tellurium dithio ligand complexes which have been analyzed theoretically. Thus *ab initio* calculations using an effective core potential approach for the core electrons of tellurium suggests that the trapezoidal geometry minimizes the repulsion between the two electron pairs of tellurium(II). The trapezoidal geometry allows a straightforward mixing of Te 5s and one 5p orbital giving rise to sp hybrid orbitals, which overlap more effectively with the sulfur orbitals. In this interpretation of the coordination geometry none of the electron pairs is in the plane of the sulfur atoms but instead above and below this plane (Figure 29).

A rather unusual but not surprising case is the structure of tellurium(II) bis(tetraphenyldithioimido-diphosphate).^{106,107} Although the ligand is bidentate, its large bite (~3.70 Å) leads to the formation of a perfectly square TeS₄ coordination sphere (Figure 30), undistorted by constraints imposed by the formation of a chelate ring, as noted above for the 1,1-dithiolato ligands. In this compound the TeS₄ group is cen-

Table 23. Molecular Dimensions of Some Planar $\text{Te}^{\text{II}}(\text{S}-\text{S})_2$ Chelates

compound	bond lengths, Å		bond angles, deg		ref(s)
	Te-S ₁	Te-S ₂	S ₁ -Te-S ₂	S ₁ -Te-S ₃	
 molecule I molecule II	2.675 2.673 2.699	2.699 2.691 2.752	86.05 87.54 86.73	93.95 92.46	106, 107 109
	2.501 2.482 (Te-S ₃)	3.104 2.971 (Te-S ₄)	86.29 126.70 (S ₂ -Te-S ₄)	86.29 (S ₃ -Te-S ₄)	110

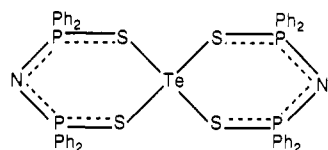
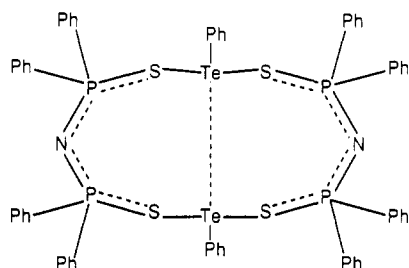
Figure 30. The square TeS_4 coordination sphere in tellurium(II) bis(tetraphenyldithioimidodiphosphinate).

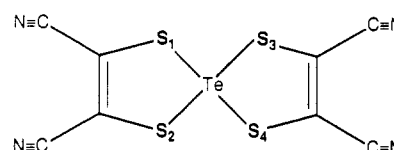
Figure 31. The structure of dimeric phenyltellurium(II) tetraphenyldithioimidodiphosphinate.

triosymmetric (planar) and the Te-S bond lengths are nearly equal (average 2.685 Å), and so are the P-S bonds. The unit cell contains two independent molecules and their dimensions are given in Table 23. The asymmetry of the TeS_4 coordination sphere is negligible. Thus, owing to the large bite, this ligand behaves like having independent donor sulfur sites and the resulting square planar geometry is similar to that found with monodentate sulfur ligands.

With the same ligand, phenyltellurium units form a dimeric macrocyclic compound $[\text{PhTe}(\text{SPPPh}_2\text{NPPPh}_2\text{S})_2]$ with a transannular $\text{Te}\cdots\text{Te}$ secondary bonding interaction (3.775 Å) and distorted square planar coordination around tellurium (Figure 31) similar to that described in section B.2.c. The Te-S bonds are nonequivalent (2.557 and 2.843 Å) but nearly collinear ($\text{S}-\text{Te}-\text{S}$ 174.28°).¹⁰⁸ The Te-S bonds form a right angle with the Te-C_{Ph} bond (89.53° and 84.74°). The large bite of this ligand appears to be responsible for the peculiar structure of this compound. The coordination geometry of tellurium is related to that of the T-shaped complexes observed with monodentate thio ligands.

In the $[\text{Te}(\text{S}_5)_2]^{2-}$ anion the coordination environment of tellurium is remarkably similar (Table 23).¹⁰⁹

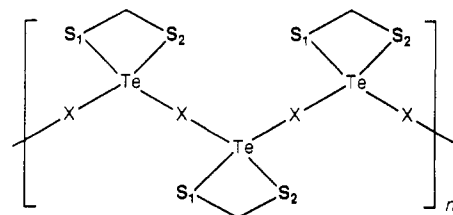
Maleonitriledithiolate, another dithio ligand with a larger bite than dithiocarbamates and xanthates, but smaller than the dithioimidodiphosphinate, forms a

Figure 32. The TeS_4 coordination sphere in bis(maleonitriledithiolato)tellurium(II).

distorted trapezoidal geometry (Figure 32).¹¹⁰ The average ligand bite of this dithiolate is 3.34 Å. The bond distances and angles are listed in Table 23.

c. Four-Coordinate, Trapezoidal Complexes with TeS_2X_2 Units

The reaction of tellurium(II) ethylxanthate with bromine produced the first compounds with this coordination skeleton. The compounds are polymers with halogen bridges, connecting the trapezoidal units through shared vertices (Figure 33).^{111,112} The only such compound structurally investigated so far seems to be $[\text{Te}(\text{S}_2\text{COEt})\text{Br}]_n$ and the molecular dimensions are listed in Table 24.

Figure 33. The tellurium environment in polymeric $[\text{Te}(\text{S}_2\text{COEt})\text{Br}]_n$.Table 24. Molecular Dimensions of Polymeric $[\text{Te}(\text{S}_2\text{COEt})\text{Br}]_n$

compound	bond lengths, Å	bond angles, deg	ref
$[\text{Te}(\text{S}_2\text{COEt})\text{Br}]_n$	Te-S ₁ 2.471	S ₁ -Te-S ₂ 128.40	111, 112
	Te-S ₂ 2.524	S ₁ -Te-Br ₁ 81.39	
	Te-Br ₁ 3.052	S ₂ -Te-Br ₂ 79.00	
	Te-Br ₂ 2.895	Br ₁ -Te-Br ₂ 128.40	
	Te ₁ ...Te _{1'} 3.797	Te-Br-Te 79.31	

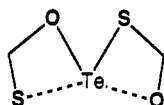
d. Four-Coordinate, Trapezoidal Complexes with TeS_2O_2 Units

Unsymmetrical bidentate chelating ligands with one sulfur and one oxygen donor site, such as thiocarboxy-

Table 25. Molecular Dimensions of TeS₂NC and Related Compounds

compound	bond lengths, Å			bond angles, deg				ref
	Te–S ₁	Te–S ₂	Te–N	bite S ₁ –Te–S ₂	N–Te–C	C–Te–S ₁	axial N–Te–S ₁	
PhN ₂ C ₆ H ₄ TeS ₂ CNMe ₂ (Figure 35a)	2.568	3.225	2.340	60.9	72.5	89.8	136.3	114
C ₆ H ₅ NC ₆ H ₄ TeS ₂ CNMe ₂ I (Figure 35b) ^a II	2.569	3.222	2.365	not given	74.5	90.3	163.7	115
[PhN ₂ C ₆ H ₄ TeSCN] ₂ (Figure 36)	2.543	3.230	2.385		74.0	89.0	162.8	116
	2.672		2.243		74.2	92.6	166.8	116
	(SCN)		3.535					
C ₆ H ₄ NC ₆ H ₄ TeS ₂ CNMe ₂ (Figure 37)	2.518	3.667 ^b	2.354		74.4	95.0	167.6	117

^a Two independent molecules in the unit cell. ^b Close to the sum of the van der Waals radii of Te and S.

Figure 34. The TeS₂O₂ environment in [Te(SOCPH)₂].

lates, have been little used in tellurium(II) chemistry. The only structure of this type known seems to be that of tellurium(II) bis(thiobenzoate), Te(SOCPH)₂.¹¹³ The molecule contains two ligands attached to tellurium through tellurium–sulfur primary bonds, with formation of two additional secondary Te...O bonds (Figure 34). The interatomic distances are Te–S 2.372 Å and Te...O 3.242 Å, and the S–Te–S bond angle is 103.1°. ¹¹³

e. Four-Coordinate Complexes with Te^{II}S₂NC Units and Related Species

The coordination unit TeS₂NC is found in some aryltellurium dithiocarbamates containing a donor nitrogen site in the side chain of the phenyl group as illustrated by (dimethyldithiocarbamato)[2-(phenylazo)phenyl-*C,N'*]-tellurium(II)¹¹⁴ and (dimethyldithiocarbamato)[2-(2-quinolyl)phenyl]tellurium(II)¹¹⁵ (Figure 35). Both compounds share the same type of nearly planar central core TeS₂NC. The coordination geometry can be described as distorted trigonal planar by disregarding the Te...S₂ secondary bonding or, alternatively, as a pseudo trigonal bipyramidal arrangement with the N–Te–S₁ bonds forming the axial fragment and the carbon atom of the phenyl group occupying an equatorial position. Two stereochemically active lone pairs would complete the equatorial plane and the S₂ atom is in a plane bisecting the angle between the lone pairs. Such an interpretation is supported by the nearly collinear N–Te and Te–S₁ bonds (see Table 25 for bond angles and interatomic distances) and by the perpendicularity of the Te–S₁ and Te–C_{Ph} bonds. A distortion is imposed, however, by the presence of a five-membered chelate ring, with an N–Te–C bond angle of ~73°.

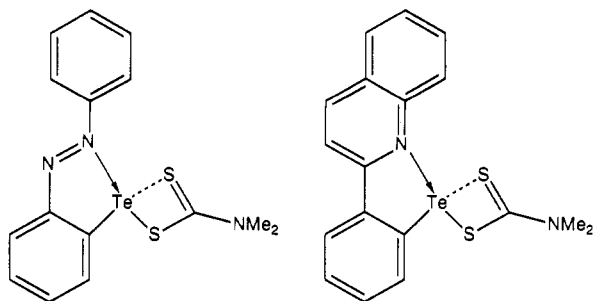
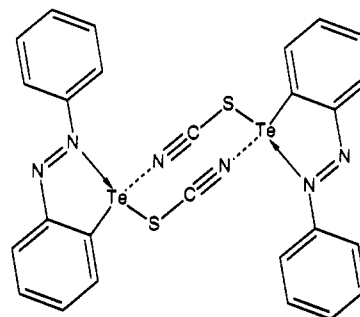
Figure 35. The structures of tellurium(II) dithiocarbamates with a Te^{II}S₂NC core.

Figure 36. The structure of [(phenylazo)phenyl]tellurium(II) thiocyanate.

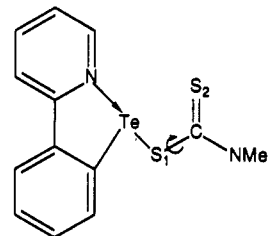


Figure 37. The structure of [2-pyridylphenyl]tellurium(II) dithiocarbamate, showing the twist of the sulfur ligand out of the molecular plane.

If a thiocyanato group replaces the dithiocarbamate, only one sulfur atom is available, but the fourth coordination site is occupied by the nitrogen atom of the thiocyanato group of a neighboring molecule. This type of structure is found in [2-(phenylazo)phenyl-*C,N'*]-thiocyanatotellurium(II)¹¹⁶ (Figure 36). The linear thiocyanate group is nearly perpendicular to the plane of the molecule (Te–S–CN 98.4°) and connects two molecules into a dimer.

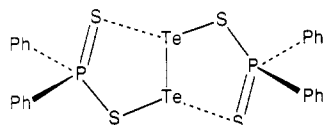
A peculiar situation occurs in (dimethyldithiocarbamato)[2-(2-pyridyl)phenyl]tellurium(II)¹¹⁷ (Figure 37). The dithiocarbamate ligand is no longer in the same plane with the aromatic rings of the molecule like the compounds shown in Figures 35 and 36. The planar ligand is twisted at an angle of 72.7° relative to the molecular plane like the SCN group in [2-(phenylazo)phenyl-*C,N'*]-thiocyanatotellurium(II) (Figure 36). This twist reduces the secondary Te...S₂ interaction almost completely as reflected in the interatomic distance Te...S₂ of 3.667 Å, which is near the van der Waals distance.

3. Tellurium(I) Complexes

The formal +1 oxidation state is present in compounds containing a Te–Te bond, and this class is represented mainly by diorganoditellurides, R–Te–Te–

Table 26. Molecular Dimensions of the Mixed-Valence Dinuclear Compound $\text{Te}_2(\text{S}_2\text{CNPr}^i_2)_3\text{I}_3$

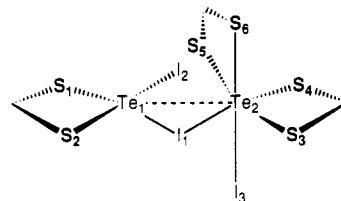
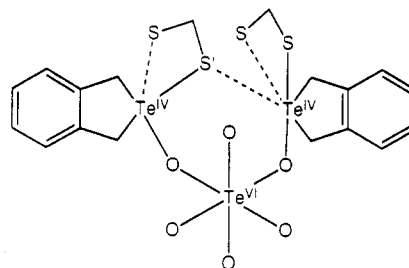
compound	bond lengths, Å	bond angles, deg		ref
		around Te(II)	around Te(IV)	
$\text{Te}_2(\text{S}_2\text{CNPr}^i_2)_3\text{I}_3$	$\text{Te}_1\text{-S}_1$ 2.440	$\text{S}_1\text{-Te}_1\text{-S}_2$ 70.3	$\text{S}_3\text{-Te}_2\text{-S}_4$ 69.6	119
	$\text{Te}_1\text{-S}_2$ 2.556	$\text{I}_1\text{-Te}_1\text{-S}_1$ 143.5	$\text{S}_3\text{-Te}_2\text{-S}_5$ 143.7	
	$\text{Te}_2\text{-S}_3$ 2.635	$\text{I}_1\text{-Te}_1\text{-S}_2$ 73.2	$\text{S}_3\text{-Te}_2\text{-S}_6$ 91.4	
	$\text{Te}_2\text{-S}_4$ 2.478	$\text{I}_2\text{-Te}_1\text{-S}_1$ 78.6	$\text{S}_4\text{-Te}_2\text{-S}_5$ 79.0	
	$\text{Te}_2\text{-S}_5$ 2.578	$\text{I}_2\text{-Te}_1\text{-S}_2$ 148.9	$\text{S}_4\text{-Te}_2\text{-S}_6$ 89.5	
	$\text{Te}_2\text{-S}_6$ 2.552	$\text{I}_1\text{-Te}_1\text{-I}_2$ 137.9	$\text{S}_5\text{-Te}_2\text{-S}_6$ 70.0	
	terminal $\text{Te}_1\text{-I}_2$ 3.013		$\text{I}_1\text{-Te}_2\text{-S}_3$ 71.4	
	terminal $\text{Te}_2\text{-I}_3$ 2.973		$\text{I}_1\text{-Te}_2\text{-S}_4$ 140.4	
	bridging $\text{Te}_1\text{-I}_1$ 3.338		$\text{I}_1\text{-Te}_2\text{-S}_5$ 133.9	
	bridging $\text{Te}_2\text{-I}_1$ 3.368		$\text{I}_1\text{-Te}_2\text{-S}_6$ 84.7	
			$\text{I}_3\text{-Te}_2\text{-S}_3$ 106.7	
			$\text{I}_3\text{-Te}_2\text{-S}_4$ 88.8	
			$\text{I}_3\text{-Te}_2\text{-S}_5$ 90.1	
			$\text{I}_3\text{-Te}_2\text{-S}_6$ 160.0	
			$\text{I}_1\text{-Te}_2\text{-I}_3$ 108.8	
		$\text{Te}_1\text{-I}_1\text{-Te}_2$ 63.8		

**Figure 38.** The tellurium environment in $[\text{Te}_2(\text{S}_2\text{PPh}_2)_2]$.

R. Only one such example with a dithio ligand is known. Thus, the (diphenyldithiophosphinato)tellurium(I) derivative, $\text{Te}_2(\text{S}_2\text{PPh}_2)_2$, was obtained in an attempt to prepare the tellurium(II) complex $\text{Te}(\text{S}_2\text{PPh}_2)_2$. The molecular structure of the Te(I) derivative is bicyclic, with two normal (covalent, 2c-2e bonds) and two secondary (long, semibonding) $\text{Te}\cdots\text{S}$ interactions¹¹⁸ as shown in Figure 38. The ligands are twisted out of the $\text{S}_1\text{TeTeS}_1'$ plane with S_2 and S_2' on opposite sides of the Te-Te bond. The bond distances are Te-S 2.471 and 2.493 Å, $\text{Te}\cdots\text{S}$ 2.989 and 3.066 Å, Te-Te 2.723 Å, and the bond angles are Te-Te-S 91.31° and 91.53° and $\text{S}\cdots\text{Te-Te}$ 85.05° and 82.31°. The structure is unique in that the molecules form supramolecular aggregates through intermolecular weak (secondary) $\text{Te}\cdots\text{Te}$ bonds (3.514 and 3.668 Å), resulting in $\text{Te-Te}\cdots\text{Te-Te}\cdots$ chains running parallel to one of the crystal axes.¹¹⁸

4. Mixed-Valence Complexes

There is only one example known of a mixed valence $\text{Te}(\text{II})\text{-Te}(\text{IV})$ compound with thio ligands bonded to each tellurium atom. This is a dinuclear complex $\text{I}(\text{Pr}^i_2\text{-NCS}_2)\text{Te}^{\text{II}}(\mu\text{-I})\text{Te}^{\text{IV}}(\text{S}_2\text{CNPr}^i_2)_2\text{I}$, in which the two coordination centers are held together by an iodine bridge and a secondary (semibonding) $\text{Te}\cdots\text{Te}$ interaction¹¹⁹ (Figure 39 and Table 26). The compound has been obtained by allowing elemental tellurium to react with iodine in dichloromethane and then adding a solution of $\text{Te}^{\text{IV}}(\text{S}_2\text{CNPr}^i_2)_4$ in the same solvent.¹¹⁹ The unique features of the structure of this compound (Figure 39) are (a) the presence of two tellurium atoms in $\text{Te}(\text{II})$ and $\text{Te}(\text{IV})$ valence states; (b) different coordination geometries around the two tellurium atoms; (c) nearly symmetric bridging of the tellurium atoms by an iodine bridge; (d) the presence of the short $\text{Te}^{\text{II}}\cdots\text{Te}^{\text{IV}}$ contact (3.542 Å) (secondary bond). Taking into account the $\text{Te}\cdots\text{Te}$ contact the structure can be best described as a distorted pentagonal planar coordination around Te^{II} (i.e., Te_1 in Figure 39). The $\text{Te}_1\text{S}_1\text{S}_2\text{I}_1\text{I}_2$ atoms form a

**Figure 39.** The environments of the tellurium atoms in $\text{I}(\text{Pr}^i_2\text{-NCS}_2)\text{Te}^{\text{II}}(\mu\text{-I})\text{Te}^{\text{IV}}(\text{S}_2\text{CNPr}^i_2)_2\text{I}$.**Figure 40.** A fragment from the molecular structure of $\text{Te}^{\text{VI}}[\text{OTe}^{\text{IV}}\{(\text{CH}_2)_2\text{C}_6\text{H}_4\}\{\text{S}_2\text{P}(\text{OEt})_2\}]_6$ showing the coordination environment of Te^{IV} and Te^{VI} .

mean plane (maximum deviation 0.023 Å); the $\text{Te}_1\cdots\text{Te}_2$ axis makes an angle of 57.9° with this plane, thus distorting the pentagon. The pentagonal bipyramidal coordination around Te^{IV} (i.e., Te_2 in Figure 39) is determined by the $\text{Te}_2\text{S}_3\text{S}_4\text{S}_5\text{I}_1\text{Te}_1$ atoms, forming the equatorial plane (distorted by maximum deviations of up to 0.287 Å), and I_3 and S_6 in a bent axial line (160°). The distortions are caused by the small bite of the dithiocarbamate ligand and possibly by the presence of stereochemically active lone pairs (above and below the pentagonal plane around Te^{II} and between I_1 and S_5 for Te^{IV}). The tellurium-sulfur distances are all short, i.e., in the range of covalent bonds (see Table 26). Some elongation compared to the sum of covalent radii of Te and S can however be observed. For bond angles also see Table 26.

A mixed-valence complex $\text{Te}^{\text{VI}}[\text{OTe}^{\text{IV}}\{(\text{CH}_2)_2\text{C}_6\text{H}_4\}\{\text{S}_2\text{P}(\text{OEt})_2\}]_6$, in which only tellurium(IV) is bonded to sulfur, is formed by connecting the central $\text{Te}(\text{VI})$ with six $\text{Te}(\text{IV})$ units of the type shown in Figure 40 through $\text{Te}^{\text{VI}}\text{-O-Te}^{\text{IV}}$ bridges. The tellurium(IV) is bonded to two sulfur atoms of a chelating dithiophosphate (Te-S 2.722 and 3.413 Å) and by another secondary interaction ($\text{Te}\cdots\text{S}$ 3.569 Å) to a third sulfur atom from a neigh-

Table 27. Molecular Dimensions of Dimers Derived from TeS_4R_2 and TeS_4XR Units

compound	bond lengths, Å	bond angles, deg	ref
$[\text{Me}_2\text{Te}(\text{S}_2\text{COMe})_2]_2$	Te–S ₁ 2.680 Te...S ₂ 3.352 Te–S ₃ 2.566 Te...S ₄ 3.303 Te...S ₁ 3.755 (intermolecular) Te–C ₁ 2.111 Te–C ₂ 2.135	in the equatorial plane: S ₁ –Te–S ₃ 165.9 S ₂ –Te–S ₄ 75.96 axial–equatorial angles: C ₁ –Te–S ₁ 88.9 S ₁ –Te–S ₁ ' 75.17 C ₁ –Te–S ₂ 79.3 S ₃ –Te–S ₁ ' 105.56 C ₁ –Te–S ₃ 91.1 C ₁ –Te–S ₄ 85.1 transaxial angle: C ₁ –Te–S ₁ ' 163.3	121
$[4\text{-EtOC}_6\text{H}_4\text{Te}(\text{S}_2\text{CNEt}_2)_2\text{Cl}]_2 \cdot \frac{1}{2}\text{dioxane}$	Te–S ₁ 2.654 Te–S ₂ 2.697 Te–S ₃ 2.642 Te–S ₄ 2.708 Te...S ₁ ' 3.739 (intermolecular) Te–Cl 2.681 Te–C 2.139 Te...S ₁ ' 3.739	in the equatorial plane: S ₁ –Te–S ₂ 66.45 S ₃ –Te–S ₄ 66.75 S ₁ –Te–S ₃ 74.88 S ₂ –Te–S ₄ 151.63 axial–equatorial angles: C–Te–S ₁ 90.75 C–Te–S ₂ 88.05 C–Te–S ₃ 90.29 C–Te–S ₄ 87.29 C–Te–Cl 92.38	122

boring group. The coordination around Te(IV) is completed by two methylene groups of the *o*-xylyl ligand and by the bridging oxygen.¹²⁰ The mixed-valence complexes $[\text{Te}^{\text{II}}(\text{etu})_4][\text{Te}^{\text{IV}}\text{Cl}_6]$ and $\{[(\text{etu})_2\text{BrTe}^{\text{II}}(\mu\text{-Br})\text{Te}^{\text{IV}}\text{Br}(\text{etu})_2]^+\}_3\text{Br}^-[\text{Te}^{\text{IV}}\text{Br}_6]^{2-}$ were mentioned above; in both compounds only the cations contain Te–S bonds.

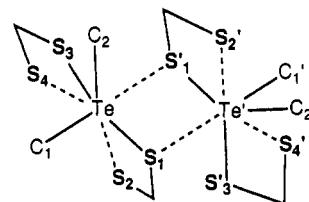
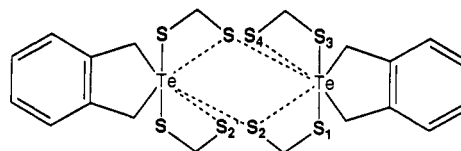
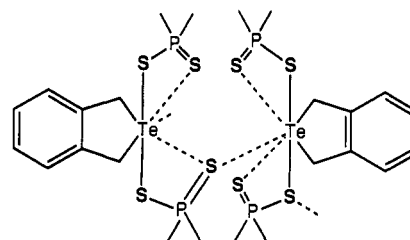
D. Supramolecular Associations through Te...S Secondary Bonding Interactions

This section discusses some tellurium–sulfur complexes in which tellurium-centered coordination units, of geometries known in mononuclear complexes, and thus capable of independent existence, associate themselves either in dimeric or polymeric structures through weak secondary Te...S interactions. It is quite possible that such interactions have been neglected in some of the earlier structure determinations, but they are worth considering separately, since their occurrence throws a new light upon the structural chemistry of tellurium–sulfur compounds. Since there is some uncertainty about the real values of the van der Waals interatomic distances, the secondary bonding interactions can sometimes be a subject of controversy. Thus long Te...S distances, which are quite close to the lowest values assigned to van der Waals interatomic distances, represent only a very weak bonding interaction.

1. Tellurium(IV) Complexes

a. Dimeric Association of Pentagonal Pyramidal TeS_4R_2 and TeS_4XR Units

Dimethylbis(dimethylxanthato)tellurium(IV), $\text{Me}_2\text{-Te}(\text{S}_2\text{COMe})_2$, exhibits a molecular geometry essentially based upon a ψ -pentagonal bipyramid, with the four sulfur atoms in equatorial positions and the two methyl groups, forming a C₁–Te–C₂ angle of 96.6°, in axial and equatorial positions (Figure 41).¹²¹ The bond lengths and angles listed in Table 27 allow the geometry to be described as pentagonal bipyramidal with the atoms S₁S₂S₃S₄C₂ in the equatorial plane. The axial position above the equatorial plane is occupied by a methyl group (C₁), while the second axial position below the equatorial plane is occupied by a sulfur atom belonging to a different molecule, which forms a very weak, long Te...S₁' secondary bond (3.755 Å). Although not explicitly stated in the original paper, it seems that two molecules are associated to form dimers. The long Te–S₁' distance is very close to some of the values assigned to van der Waals nonbonding distances which may explain why the dimerization was ignored.

**Figure 41.** Dimeric association of $\text{Me}_2\text{Te}(\text{S}_2\text{COMe})_2$ units.**Figure 42.** Dimeric association of $\text{C}_6\text{H}_4(\text{CH}_2)_2\text{Te}(\text{S}_2\text{COEt})_2$.**Figure 43.** The structure of the polymeric chain of $\text{C}_6\text{H}_4(\text{CH}_2)_2\text{Te}[\text{S}_2\text{P}(\text{OEt})_2]_2$.

A dimeric association was also observed in the compound $\text{C}_6\text{H}_4(\text{CH}_2)_2\text{Te}(\text{S}_2\text{COEt})_2$ in which strongly distorted trigonal bipyramidal coordination is displayed around tellurium (Figure 42).⁹⁶ The secondary bonds leading to dimerization (Te–S₁' 3.480 Å) are only a little longer than the intraligand Te...S bonds (Te–S₂ 3.322 Å and Te–S₄ 3.272 Å) of the anisobidentate ligand, while the primary Te–S bonds (short) exhibit normal values (Te–S₃ 2.641 Å and Te–S₁ 2.614 Å) observed in xanthates. The distortions are illustrated by the small transaxial bond angle S₁–Te–S₃ of 164.63° (instead of 180°) and other interligand S–Te–S bond angles (133.59° and 135.36°) while the angles within the chelate rings are small as expected (S₁–Te–S₂ 59.08° and S₃–Te–S₄ 59.80°).⁹⁶

The diorganotellurium derivative $\text{C}_6\text{H}_4(\text{CH}_2)_2\text{Te}[\text{S}_2\text{P}(\text{OEt})_2]_2$ forms zigzag polymeric chains, in which distorted ψ -trigonal bipyramidal units are interconnected through weak secondary Te...S bonds (3.729 Å) as depicted in Figure 43.⁹⁶ Within the coordination unit primary (2.627 and 2.621 Å) and secondary (3.493 and 3.447 Å) tellurium–sulfur bonds are observed. The strong distortions are illustrated by the transaxial S₁–

Table 28. Molecular Dimensions of Dimeric $[R_3Te^{IV}(S-S)]_2$ Complexes

compound	Te-S bond lengths, Å	bond angles, deg	ref
$[Ph_3TeS_2CNPr'_2]_2^a$	Te ₁ -S ₁ 3.095 Te ₁ -S ₄ 3.145	S ₁ -Te-C ₁ 83.1 S ₁ -Te-C ₂ 82.5 S ₁ -Te-C ₃ 172.4 S ₁ -Te-S ₄ 92.6 S ₄ -Te-C ₁ 173.6 S ₄ -Te-C ₂ 91.5 S ₄ -Te-C ₃ 76.8	123
$[Ph_3TeS_2COMe]_2$	Te ₁ -S ₁ 3.270 Te ₂ -S ₃ 3.187 Te ₁ -S ₄ 3.180 Te ₂ -S ₂ 3.179	S ₁ -Te ₁ -S ₄ 95.0 S ₂ -Te ₂ -S ₄ 95.3 S ₁ -Te ₁ -C ₁ 81.6 S ₁ -Te ₁ -C ₂ 84.0 S ₂ -Te ₁ -C ₃ 172.4 S ₄ -Te ₁ -C ₁ 175.9 S ₄ -Te ₁ -C ₂ 79.4 S ₄ -Te ₁ -C ₃ 91.9	124

^a Centrosymmetric molecule.

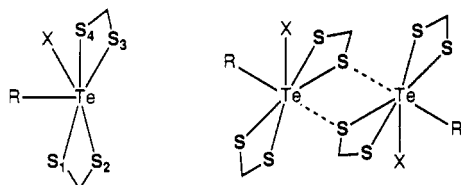


Figure 44. (Left) The ψ -pentagonal TeS_4XR unit in p -EtOC₆H₄Te(S₂CNEt₂)₂Cl and (right) association of the TeS_4XR units to form a dimer.

Te-S₃ bond angle (163.6°) and interligand S-Te-S angles of 66.3°, 130.4°, and 130.5°, whereas the S-Te-S angles within the chelate rings have the usual small values (64.13° and 64.35°). The two sulfur ligands are anisobidentate.

These two complexes (Figures 42 and 43) may alternatively be described as distorted pentagonal bipyramidal if the secondary bonds are taken into account or as distorted ψ -dodecahedral if, in addition, the lone pair is active.

A structure similar to that of $Me_2Te(S_2COMe)_2$ is observed in p -EtOC₆H₄Te(S₂CNEt₂)₂Cl· $\frac{1}{2}$ dioxane.¹²² This compound can be described as ψ -pentagonal bipyramidal with an axial lone pair (Figure 44, left), but a secondary interaction $Te \cdots S(1')$ at 3.738 Å leads to dimer formation (Table 27). In the dimer two distorted pentagonal pyramids are joined together (Figure 44, right) by two such semibonds. It is clear from the molecular dimensions that the Te-C bond is practically perpendicular to the pentagonal S₁S₂ClS₄S₃ plane. The axial angle $S_{ax} \cdots Te-C$ is 162.0° which is larger than in complexes in which this bond is intramolecular. The role of the lone electron pair in this compound is unclear. If it is considered stereochemically active, then the geometry becomes distorted ψ -dodecahedral.

b. Dimeric Association of $Te^{IV}SS'R_3$ Units

Triphenyltellurium diisopropylthiocarbamate¹²³ and methylxanthate¹²⁴ form dimeric complexes in which the dithio ligand bridges the tellurium atoms. The long $Te \cdots Te$ distance, e.g. 4.13 Å in $[Ph_3Te(S_2CNPr'_2)]_2$, shows that no actual Te-Te bond, primary or secondary, is present in this dimer, since this value is close to the sum of van der Waals radii (4.40 Å). The Te-S bonds are all rather long and unequal (Figure 45). The coordination around tellurium may be described as ψ -octahedral in the dimer, with S-Te-C and C-Te-C bond angles close to 90°. However the distortions are significant. Some molecular dimensions are given in Table 28. The more sterically crowded triphenyltellurium isobutylxanthate, $Ph_3TeS_2COBu^i$, is a monomer

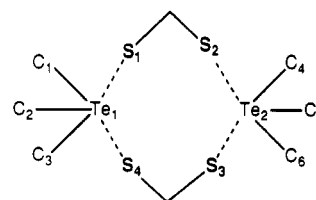


Figure 45. The tellurium environment in the dimer $[Ph_3Te(S_2CNPr'_2)]_2$.

with a weakly chelating xanthate ligand ($Te \cdots S_1$ 3.123 Å, $Te \cdots S_2$ 3.535 Å).¹²⁵

c. Dimeric and Tetrameric Association of $R_3Te^{IV}SCN$ Units

An interesting example of association through secondary bonds is displayed by triphenyltellurium thiocyanate, Ph_3TeSCN . The crystal lattice of this compound contains both dimeric $[Ph_3TeSCN]_2$ and tetrameric $[Ph_3TeSCN]_4$ ionic associations, well separated by van der Waals distances.^{125,126} In the dimer and tetramer (Figure 46) the Ph_3Te^+ cations and SCN^- anions are interconnected by long $Te \cdots S$ ($a = 3.256$ Å in the dimer; $b = 3.348$ Å and 3.527 Å in the tetramer) and $Te \cdots N$ (3.153 Å in the dimer; 3.182 Å in the tetramer) interatomic distances which are intermediate between covalent and van der Waals distances. A puckered eight-membered ring with a chair conformation is formed in the dimer, whereas the tetramer consists of two nearly planar eight-membered rings in two parallel planes, joined through a four-membered Te_2S_2 (quasi)-ring, formed through secondary bonding interactions ($c = 3.527$ Å and $d = 3.616$ Å). The dihedral angle between the planes of the eight- and four-membered rings in the tetramer is 99.9°. Five- and six-coordinate tellurium atoms in distorted square pyramidal and

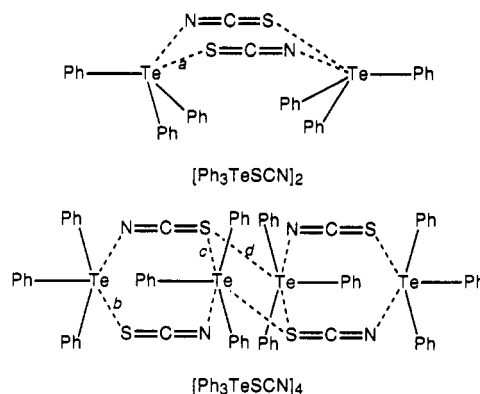
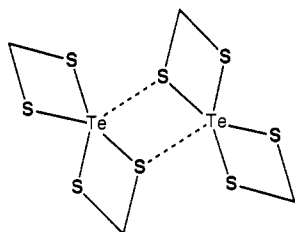


Figure 46. The structures of dimeric and tetrameric Ph_3TeSCN .

Table 29. Molecular Dimensions of Trapezoidal [Te^{II}(S-S)₂] Dimers

compound	bond lengths, Å				Te...S ₂	bond angles, deg				ref
	short Te-S ₁	long Te-S ₂	short Te-S ₃	long Te-S ₄		interlig S ₁ -Te-S ₃	intra lig S ₁ -Te-S ₂	interlig S ₂ -Te-S ₄	intra lig S ₃ -Te-S ₄	
Te(S ₂ COMe) ₂	2.510	2.841	2.499	2.846	3.513	85.18	66.2	142.29	66.33	127,128
I	2.491	2.948	2.481	2.852	3.509	83.3	65.1	144.4	67.3	129
II	2.499	2.958	2.483	2.850	3.509	83.2	64.6	145.6	66.6	129
III	2.486	2.897	2.480	2.857	3.610	83.6	65.5	144.5	66.4	130
Te(S ₂ COEt)(S ₂ CNEt ₂)	2.535	2.911	2.489	2.801	3.679	81.19	65.39	146.30	67.06	131
Te(S ₂ CNEt ₂) ₂	2.519	2.830	2.518	2.893	3.579	80.1	66.5	147.8	65.8	132
Te(S ₂ CNPr ⁿ) ₂	2.511	2.853	2.516	2.821	3.499	80.5	66.0	147.0	66.5	133
Te(S ₂ CNPr ⁱ) ₂	2.520	2.821	2.530	2.821	3.628	79.9	66.0	148.1	65.8	134
Te(S ₂ C(morph)) ₂	2.498	2.856	2.530	2.834	3.676	80.9	66.8	145.7	66.6	135
Te[S ₂ CN(C ₂ H ₄ OH) ₂] ₂	2.562	2.788	2.527	2.793	3.296	80.3	65.5	147.6	67.4	136

**Figure 47.** Dimeric association of trapezoidal TeS₄ units in Te(II) bis(xanthates) and bis(dithiocarbamates).

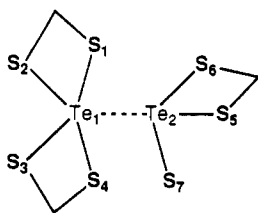
octahedral geometries are present in the two structures.^{125,126}

2. Tellurium(II) Complexes

a. Dimeric Association of Trapezoidal TeS₄ Units

Tellurium(II) exhibits a remarkable tendency to achieve five-coordination with a pentagonal planar geometry. In bis(xanthates) and bis(dithiocarbamates) this is attained through secondary interactions with the formation of dimers joined in such a way that a sulfur atom of a second trapezoid occupies the fifth position of the first trapezoid, and vice versa,¹²⁷⁻¹³⁶ as shown in Figure 47. The structural data are listed in Table 29.

A unique structure consisting of two interpenetrating trapezoids with formation of a dinuclear complex with four- and five-coordinate tellurium atoms has been discovered in the compound Te^{II}₂[S₂CN(CH₂CH₂OH)₂]₃SCN, obtained from the bis(dithiocarbamate) and potassium thiocyanate.¹³⁷ The two tellurium atoms display entirely different coordination modes. The first tellurium is coordinated by two bidentate chelating ligands, whereas the second tellurium is chelated by one bidentate ligand and coordinated by a monodentate thiocyanato group (Figure 48). The tellurium-tellurium secondary interaction at 3.221 Å is particularly worth mentioning as an interesting feature of this structure. The molecular dimensions are listed in Table 30.

**Figure 48.** The tellurium environments in Te^{II}₂[S₂CN(CH₂CH₂OH)₂]₃SCN.**Table 30. Molecular Dimensions of Te^{II}₂[S₂CN(CH₂CH₂OH)₂]₃SCN**

compound	bond lengths, Å		bond angles, deg	ref	
Te ₂ [S ₂ CN(C ₂ -H ₄ OH) ₂] ₃ ·(SCN)	Te ₁ -S ₁	2.787	Te ₂ -S ₅	2.523	intra ligand angles: 137 S ₁ -Te ₂ -S ₂ 67.0 S ₃ -Te ₁ -S ₄ 65.9 S ₅ -Te ₂ -S ₆ 70.4 interligand angles: S ₁ -Te ₁ -S ₄ 145.4 S ₆ -Te ₂ -S ₇ 145.9 other angles: Te ₁ -Te ₂ -S ₅ 152.2 Te ₁ -Te ₂ -S ₇ 131.4 S ₄ -Te ₁ -Te ₂ 69.5
	Te ₁ -S ₂	2.570	Te ₂ -S ₆	2.527	
	Te ₁ -S ₃	2.852	Te ₂ -S ₇	2.923	
	Te ₁ -S ₄	2.553			
	Te ₁ ...Te ₂	3.221			

b. Polymeric Associations of Angular TeS₂ and TeSR Units

The tendency of tellurium(II) to achieve four-coordination results in supramolecular associations of some Te(S-S)₂ (S-S = bidentate dithio ligand) type complexes. Thus, some potentially bidentate ligands choose to coordinate to a tellurium atom only as a monodentate ligand through one sulfur atom, leaving the other sulfur atom to establish secondary interactions with a tellurium atom of another molecule. This may lead to supramolecular polymers.

In the particular case of phosphorodithioates, Te-[S₂P(OR)₂]₂ (R = Me, Et)^{138,139} the coordination unit becomes trapezoidal (Figure 49) as a result of secondary coordination. The molecular dimensions are listed in Table 31.

In monoorganotellurium xanthates, [4-ROC₆H₄Te{S₂COMe}]_n, with R = Me, Et (refs 54 and 140) double-strand polymeric chains formed with the participation of secondary interactions are found as illustrated schematically in Figure 50. Some molecular dimensions in the double-strand polymeric chains are listed in Table 32.

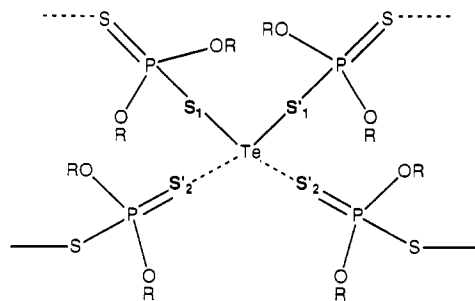
**Figure 49.** Polymerization of [Te{S(S)P(OR)₂}]₂ (R = Me).

Table 31. Molecular Dimensions of $[\text{Te}(\text{S}_2\text{P}(\text{OR})_2)_2]_n$ Derivatives

compound	bond lengths, Å		bond angles, deg		ref
	intramolecular	intermolecular	$\text{S}_1\text{-Te-S}_1'$	$\text{S}_2\text{-Te-S}_2'$	
	Te-S_1	$\text{Te}\cdots\text{S}_2$			
$[\text{Te}\{\text{S}_2\text{P}(\text{OMe})_2\}_2]_n$	2.440	3.306	98.3	85.5	138
$[\text{Te}\{\text{S}_2\text{P}(\text{OEt})_2\}_2]_n^a$					139
molecule I	2.420, 2.430	3.379, 3.311	100.18	70.24	
molecule II	2.435, 2.385	3.541, 3.209	96.56	101.00	
molecule III	2.424, 2.421	3.294, 3.459	95.23	91.70	

^a Three independent molecules in the unit cell.

Table 32. Molecular Dimensions of $[4\text{-ROC}_6\text{H}_4\text{TeS}_2\text{COMe}]_n$ Derivatives

compound	bond lengths, Å			bond angles, deg		ref
	primary Te-S_1	intrastrand $\text{Te}\cdots\text{S}_2$	interstrand $\text{Te}\cdots\text{S}_2'$	R-Te-S_1	$\text{S}_1\text{-Te-S}_2'$	
	$[4\text{-MeOC}_6\text{H}_4\text{TeS}_2\text{COMe}]_n$	2.404	3.467	3.622	97.24	
$[4\text{-EtOC}_6\text{H}_4\text{TeS}_2\text{COMe}]_n$	2.404	3.451	3.707	96.53	101.36	54

Table 33. Molecular Dimensions of $[\text{p-ROC}_6\text{H}_4\text{TeS}_2\text{P}(\text{OR})_2]_n$ Derivatives

compound	bond lengths, Å		bond angles, deg		ref
	Te-S	$\text{Te}\cdots\text{S}$	C-Te-S_1	$\text{S}_1'\text{-Te-S}_2$	
	$[4\text{-MeOC}_6\text{H}_4\text{TeS}_2\text{P}(\text{OMe})_2]_n$	2.443	3.262	94.89	
$[4\text{-EtOC}_6\text{H}_4\text{TeS}_2\text{P}(\text{OMe})_2]_n$	2.439	3.309	94.75	172.41	54

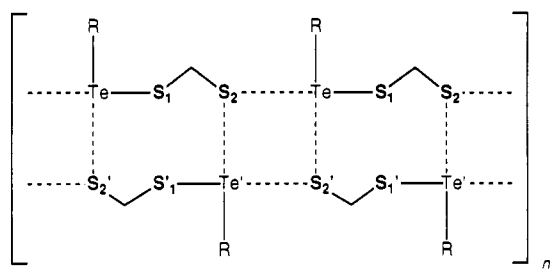


Figure 50. Double-strand polymeric chains found in monoorganotellurium xanthates $[4\text{-ROC}_6\text{H}_4\text{Te}(\text{S}_2\text{COMe})]_n$.

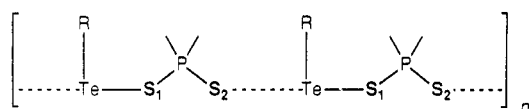


Figure 51. Single-strand polymeric chains found in monoorganotellurium phosphorodithioates, $[\text{RTeS}_2\text{P}(\text{OR}')_2]_n$.

Monoorganotellurium phosphorodithioates, $\text{RTeS}(\text{S})\text{P}(\text{OR}')_2$, with $\text{R} = \text{Me}$ or Et and $\text{R}' = \text{Me}$, also form supramolecular associates through secondary interactions from the doubly bonded sulfur ($\text{P}=\text{S}$) of one molecule to the tellurium atom of a neighboring molecule, resulting in single-strand chain polymers (Figure 51).^{54,141} Some molecular dimensions of such chains are listed in Table 33.

A different type of structure was found for the closely related compound $[\text{PhTeS}_2\text{PPh}_2]_n$, which exhibits a novel type of coordination for a dithiophosphorus ligand, namely through only one of its sulfur atoms as shown schematically in Figure 52. The second sulfur atom of each ligand, doubly bonded to phosphorus ($\text{P}=\text{S}$ 1.944 Å), is not participating in coordination. The coordination geometry at tellurium is again T-shaped ($\text{S-Te}\cdots\text{S}$ 173.1°, R-Te-S 98.9°, and $\text{R-Te}\cdots\text{S}$ 87.9°), and the chain is bent at sulfur. The tellurium atom forms primary short (Te-S 2.406 Å) and secondary long ($\text{Te}\cdots\text{S}$ 3.383 Å) tellurium-sulfur bonds.¹⁴²

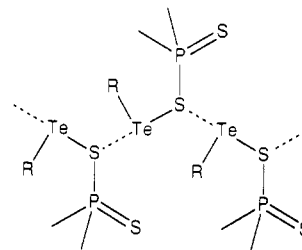


Figure 52. The structure of the polymeric chain in $[\text{PhTeS}_2\text{PPh}_2]_n$.

E. Overview and Conclusions

An overview of the structural chemistry of tellurium compounds with sulfur ligands clearly shows some preferences for specific coordination geometries of various oxidation states of tellurium. The multiple factors which operate in the structural chemistry of tellurium, briefly mentioned in the Introduction, suggest that the structures of tellurium compounds with sulfur ligands still remain largely unpredictable in spite of some regularities which may emerge. However, there are three questions of importance in relation to the stereochemistry of tellurium complexes with sulfur ligands, namely the coordination geometry, the interatomic distances reflecting bond strengths, and the stereochemical activity of the lone pairs.

The structural data about tellurium complexes of sulfur ligands are summarized in Table 34 (simple compounds with monodentate ligands), Table 35 (simple compounds with bidentate ligands), and Table 36 (supramolecular associations). It is obvious that the great structural diversity of this type of compound is greatly influenced by the oxidation state of tellurium (strongly influencing the coordination number and geometry), by the nature of the ligands (monodentate or bidentate with small or large bite), and by the presence of only one or of several types of ligands in the primary coordination sphere of tellurium.

Table 34. Summary of Tellurium–Sulfur Interatomic Distances Correlated with Coordination Geometries in Complexes of Monodentate Sulfur Ligands^a

type of compound	CN of Te	coordination geometry	Te–S interatomic distances		examples in table
			shortest	longest	
Tellurium(IV)					
[TeS ₂ X ₄]	6	<i>trans</i> -octahedral (S <i>trans</i> S)	2.65	2.73	2
[TeS ₂ X ₄]	6	<i>trans</i> -octahedral (S <i>cis</i> S)		2.63	2
Tellurium(II)					
[TeS ₄]	4	square planar	2.57	2.74	3
[TeS ₂ S' ₂]	4	square planar (S <i>trans</i> S)	2.65	2.72	3
[TeS ₂ S' ₂]	4	square planar (S <i>trans</i> S')	2.52	2.87–2.95	3
[TeS ₂ (μ-S) ₂] ⁴⁺	4	square planar dimeric (S <i>trans</i> S)	2.44–2.55 (terminal)	2.83–3.04 (bridging)	4
[TeS ₂ X ₂]	4	square planar (S <i>trans</i> S)	2.64	2.76	5
[TeS ₂ X ₂]	4	square planar (S <i>cis</i> S, <i>trans</i> X)	2.46	2.61	5
[TeS ₂ (μ-X)] ₂ ⁴⁺	4	square planar dimeric (S <i>trans</i> X)		2.48	6
[(TeS ₂ X) ₂ (μ-X)] ⁺	4	square planar binuclear (S <i>trans</i> X)		2.48 (terminal)	7
[TeS ₂ (μ-X)] _n ⁿ⁺	4	square planar polymeric (S <i>trans</i> X)		2.47 (terminal)	7
[TeSX(μ-X)] ₂	4	square planar dimeric (S <i>trans</i> X)		2.42–2.74 (terminal)	8
[RTeS ₂]	3	T-shaped (S <i>trans</i> S)	2.61	2.66	9
[RTeSX]	3	T-shaped (S <i>trans</i> X)	2.50	2.61	9
[TeS ₂]	2	angular		2.36–2.41	10

^a Abbreviations used in Tables 34 and 35: CN = coordination number; S = monodentate sulfur–donor ligands (e.g., thioureas); X = halogen; R = alkyl or aryl group; S–S = bidentate sulfur ligand; S–O = bidentate sulfur–oxygen ligand.

Table 35. Summary of Tellurium–Sulfur Interatomic Distances Correlated with Coordination Geometries in Complexes of Bidentate Sulfur Ligands

type of compound	CN of Te	coordination geometry	Te–S interatomic distances		examples in table
			shortest	longest	
Tellurium(IV)					
[Te(S–S) ₄]	8	dodecahedral	2.63 Å	2.86 Å	11
[Te(S–S) ₃ S']	7	pentagonal bipyramidal		2.46 Å	12
[Te(S–S) ₃ X]	7	pentagonal bipyramidal		2.79 (Te–S), 2.96 Å (Te–S')	13
[Te(S–S) ₃ R]	7	pentagonal bipyramidal	other Te–S 2.59 Å	Te–S <i>trans</i> to X: 2.46 Å 2.87 Å	13
[Te(S–S) ₂ X ₂]	6	<i>ψ</i> -trigonal bipyramidal ^a	2.52 Å	3.44 Å <i>trans</i> to R 2.67 Å	14
[Te(S–S) ₂ X] ⁺	6	<i>ψ</i> -trigonal bipyramidal ^a	2.44 Å	2.62 Å	15
[Te(S–S) ₂ R ₂]	6	<i>ψ</i> -trigonal bipyramidal ^a	2.60 Å	3.38 Å	16
[Te(S–S) ₂ RX]	6	pentagonal pyramidal	2.62 Å	2.72 Å	Figure 18
[Te(S–S) ₂ X ₄] [–]	6	distorted octahedral	2.48 Å	2.53 Å	17
[Te(S–S) ₂ X ₂ R]	5	<i>ψ</i> -octahedral	2.63 Å	2.73 Å	18
[Te(S–S)XR ₂]	5	trigonal bipyramidal	2.48 Å (<i>trans</i> X)	3.18 Å	19
[Te(S–O) ₂]	4	<i>ψ</i> -trigonal bipyramidal		2.38 Å	20
Tellurium(II)					
[Te(S–S) ₂ S']	5	planar pentagonal	2.50 Å	3.06 Å	21
[Te(S–S) ₂ N]	5	planar pentagonal	2.54 Å	2.84 Å	21
[Te(S–S) ₂] small bite	4	planar trapezoidal	2.46 Å	2.94 Å	22
[Te(S–S) ₂] large bite	4	square planar	2.67 Å	2.75 Å	23
[Te(S–S) ₂] large bite	4	square planar	2.48 Å	3.10 Å	23
[Te(S–S)(μ-X)] _n	4	planar trapezoidal	2.47 Å	2.52 Å	24
[Te(S–O) ₂]	4	non-planar irregular	2.37 Å	Te...O 3.24 Å	Figure 34
[TeS ₂ NC]	4	planar trapezoidal	2.54 Å (<i>trans</i> N)	3.23 Å (<i>trans</i> C)	25
Tellurium(I)					
[Te(Te)S ₂] ₂	3	distorted T-shaped	2.47 Å	3.01 Å	Figure 38

^a Weakly bonded sulfur or halogen atoms are not considered as occupying the vertices of the coordination polyhedron.

Table 36. Summary of Tellurium-Sulfur Interatomic Distances in Supramolecular Associated Compounds

type of compound	coordination geometry	interatomic distances, Å			examples in table
		intramolecular		inter-molecular	
		shortest	longest		
Tellurium(IV)					
[Te(S-S) ₂ R ₂] ₂	pentagonal bipyramidal	2.57	3.35	3.75	27
[Te(S-S) ₂ RX] ₂	pentagonal bipyramidal	2.56	2.71	3.74	27
[Te(S-S)R ₃] ₂	ψ-octahedral	3.01-3.27		3.18-3.70	28
Tellurium(II)					
[Te(S-S) ₂] ₂	pentagonal planar	2.48-2.56	2.79-2.96	3.30-3.68	29
[Te(S-S) ₂] _n (dithiophosphates)	square planar	2.38	2.43	3.21-3.54	31
[Te(S-S)R] _n (double-strand xanthate)	square planar	2.40	intrastrand: 3.47 interstrand: 3.71		32
[Te(S-S)R ₂] ₂	T-shaped	2.44		3.31	33
[Te(S-S)R] _n (single-strand dithiophosphinate)	T-shaped	2.406		3.383	Figure 52

With monodentate ligands tellurium(IV) forms octahedral complexes with interatomic distances in the range corresponding to 3c-4e bonds (2.68 ± 0.5 Å). The Te-S bond is shortened when the sulfur atom is *trans* to a halogen and elongated when it is *trans* to another sulfur.

Tellurium(II) generally forms square planar complexes in which the Te-S bond lengths are in the range of normal covalent bonds or slightly longer. However, interatomic distances in the range expected for 3c-4e bonds are also observed as a result of the *trans* influence. Even in TeS₄-type complexes, the four Te-S distances are not identical, which is more evident in the TeS₂S'₂-type complexes. The nonidentical *trans* influence of the two sulfur ligands produces significant differences in the bond lengths. When the sulfur ligand is *trans* to a halogen or to ligands with weak *trans* influences and the Te-S bond is nonbridging (terminal), the Te-S distance is shorter ($\sim 2.45 \pm 0.03$ Å) in the range of normal covalent bonds. With an organic group attached to tellurium (phenyl or other aryl in the known cases) the latter has a strong *trans* influence and weakens the bond opposite to it thereby resulting in complete expulsion of the ligand and thus leading to T-shaped geometries with three-coordinate tellurium. Dicoordinate tellurium(II) complexes are known only for thiosulfato and thiosulfonato ligands. These compounds exhibit S-Te-S bond angles slightly larger than 90° and the shortest Te-S bonds (2.36-2.41 Å) are comparable to those observed (2.34-2.35 Å) in the inorganic salts of the trithiotellurite anions, i.e., Ba[TeS₃]·2H₂O, (NH₄)₂[TeS₃],¹⁴³ Ba[TeS₃],¹⁴⁴ and complexes like Cs₆[Cu₂(S₆)₂(TeS₃)₂] in which the trigonal pyramidal [TeS₃]²⁻ anion contains sulfur atoms attached to tellurium(IV) as terminal Te-S- units.¹⁴⁵

Bidentate sulfur ligands exhibit a greater structural diversity in their tellurium coordination chemistry. Small bite dithiolato ligands such as dithiocarbamates, xanthates, and dithiophosphates impose a close approach of a sulfur atom to the central tellurium atom and usually a strong anisobidentate coordination with short and long Te-S distances. Tellurium(IV) complexes with bidentate sulfur ligands usually exhibit eight-coordination with a dodecahedral (bisdisphenoidal) geometry and very unsymmetrical Te-S bonds (~ 2.6 and 2.9 Å). Successive replacement of bidentate ligands with monodentate ligands or organic groups reduces the tellurium coordination number in the sequence dodecahedron (coordination number 8) →

pentagonal bipyramid (coordination number 7) → pentagonal pyramid or distorted octahedron (coordination number 6) → trigonal bipyramid (coordination number 5) → ψ-trigonal bipyramid (coordination number 4). The detailed coordination geometry appears to be governed by the tendency to reduce the electron pair repulsion. The lone pair, when stereochemically active, plays an important role and some of the unusual observed bond angles may arise from stereochemical activity of the lone pair.

The *trans* influence also plays an important role in the stereochemistry of tellurium(IV) complexes of sulfur ligands. Thus when a sulfur atom is in a *trans* position to a halogen, the Te-S bonds are shortened to 2.44-2.53 Å, whereas when a sulfur atom is *trans* or nearly *trans* to another sulfur atom, the Te-S bonds are slightly longer. Substantial elongation of the Te-S bond occurs when the sulfur donor is *trans* to a carbon ligand such as an aryl group. In many cases aryl groups have such a strong *trans* influence that they can even expel the ligand in the *trans* position.

In tellurium(II) complexes of bidentate ligands the highest observed coordination number is five corresponding to a planar pentagonal coordination geometry with the two lone pairs of Te(II) located on the C₅ axis on the two opposite sides of the pentagon. The dithio ligand is anisobidentate (unsymmetrically coordinated) with short primary (~ 2.5 Å) and long secondary (3.0 ± 0.2 Å) Te-S bonds. By removing a vertex from the pentagon a planar trapezoidal geometry results again with short (~ 2.45 Å) and long (~ 3.0 Å) Te-S bonds. This coordination is commonly encountered in four-coordinate Te(II) complexes with small bite ligands. When the dithio ligand has a large bite and can form six-membered chelate rings, the tellurium coordination becomes square planar with less or no strain and somewhat averaged Te-S bond lengths (2.67-2.75 Å). The formation of a five-membered chelate ring, even with a large bite bidentate ligand, is not sufficient to induce square planar coordination and again the planar trapezoidal geometry with unsymmetrical Te-S bonds (2.48 and 3.1 Å) is unexpectedly observed for maleonitriledithiolate.

The lone pairs of electrons (one in Te(IV) compounds and two in Te(II) compounds) appear sometimes to be stereochemically active, particularly in lower oxidation states. Attempts to correlate lone pair stereochemical activity with the "softness" of the ligands¹⁴⁶ may help to explain some of the structural features of tellurium

complexes, but the question appears to be more complicated. A newer approach, based on the valence shell electron repulsion theory (VSEPR), explains some peculiarities observed in the structures of tellurium-sulfur complexes.¹⁴⁷

Supramolecular associations of tellurium-sulfur complexes frequently occur, probably because of the tendency of tellurium to attain the coordination numbers and geometries found in "simple" compounds which are typical for a given donor set configuration. In supramolecular compounds the building units display bond lengths in the range of normal covalent primary Te-S bonds (~2.4 Å) and in some cases intraunit secondary Te...S bonds in the range 2.7 to 3.0 Å. Longer Te-S distances are observed when the sulfur is opposite to an aromatic group. Thus in R₃Te(S-S) dimeric derivatives the accumulation of aromatic R groups produces such a strong *trans* influence to weaken all Te-S bonds so that no primary Te-S bonds remain and the two R₃Te moieties are bridged by two dithio ligands connected only through secondary Te...S bonds (3.01-3.70 Å). The intermolecular secondary tellurium-sulfur bonds which connect the molecular building blocks into supramolecular structures are all long in the range 3.2-3.7 Å and sometimes reflect rather weak interactions. However, these relatively weak tellurium-sulfur interactions are strong enough to determine certain structural features observed in the solid state such as the organization of the building blocks in the crystal structure.

The information presented in this review reveals that the chemistry of tellurium complexes with sulfur ligands is a fascinating but underdeveloped area which deserves more attention from synthetic chemists as well as structural and theoretical chemists. We hope that this review will indicate some neglected areas of interest for further development such as R₃Te derivatives, compounds with large bite chelating ligands, compounds with different donor atoms in a ligand set (S/O, S/N, S/O/N, etc.), new dithio ligands (e.g., dithiocarboxylates, dithioenolates, dithioarsenates, etc.), and compounds with mixed ligands. The recent interest in tellurium chemistry promises exciting results in the near future.

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Note Added in Proof

After the acceptance of this manuscript the structures of Me₂Te(S₂CNMe₂)₂, (*p*-MeOC₆H₄)₂Te(S₂CNMe₂)₂,¹⁴⁸ and TeI₂(S₂CNEt₂)₂¹⁴⁹ were reported.

F. Literature References

- (1) Foss, O. *Pure Appl. Chem.* 1970, 24, 31.
- (2) Husebye, S. *Proceedings of the Fourth International Conference on the Organic Chemistry of Selenium and Tellurium*; Berry, F. J., McWhinnie, W. R., Eds.; The University of Aston: Birmingham, England, 1983; p 298.
- (3) Husebye, S. *Phosphorus Sulfur* 1988, 38, 271.
- (4) Foss, O. *Acta Chem. Scand.* 1962, 16, 779.
- (5) Alcock, N. W. *Adv. Inorg. Chem. Radiochem.* 1972, 15, 1.
- (6) Gillespie, R. J. *Angew. Chem., Int. Ed. Engl.* 1967, 6, 819. Gillespie, R. J. *J. Chem. Educ.* 1970, 47, 18.
- (7) Gillespie, R. J.; Hargittai, I. *The VSEPR Model of Molecular Geometry*; Allyn and Bacon: New York, 1991.
- (8) Hoskins, B. F. *Aust. J. Chem.* 1976, 29, 2541.
- (9) Glidewell, C. *Inorg. Chim. Acta* 1976, 20, 113.
- (10) Saethre, L. J.; Gropen, O. *Can. J. Chem.* 1992, 70, 348.
- (11) Glidewell, C. *Inorg. Chim. Acta* 1979, 36, 135.
- (12) Pauling, L. *The Nature of the Chemical Bond*; Cornell University Press: Ithaca, New York, 1960; p 224.
- (13) Bondi, A. J. *Phys. Chem.* 1964, 68, 441.
- (14) Esperas, S.; George, J. W.; Husebye, S.; Mikalsen, O. *Acta Chem. Scand.* 1975, A29, 141.
- (15) Husebye, S.; George, J. W. *Inorg. Chem.* 1969, 8, 313.
- (16) Von Deuten, K.; Schnabel, W.; Klar, G. *Cryst. Struct. Commun.* 1979, 8, 221.
- (17) Von Deuten, K.; Schnabel, W.; Klar, G. *Cryst. Struct. Commun.* 1979, 8, 679.
- (18) Burdett, J. K. *Molecular Shapes*; Wiley: New York, 1980; p 84.
- (19) Foss, O.; Maartmann-Moe, K. *Acta Chem. Scand.* 1987, A41, 310.
- (20) Fosheim, K.; Foss, O.; Scheie, A.; Solheimsnes, S. *Acta Chem. Scand.* 1965, 19, 2336.
- (21) Barnard, P. W. C.; Donaldson, J. D.; Grimsey, R. M. A.; Dennes, G.; Russo, U.; Calogero, S. *Inorg. Chim. Acta* 1981, 51, 217.
- (22) Valle, G.; Calogero, S.; Russo, U. *Cryst. Struct. Commun.* 1980, 9, 649.
- (23) Foss, O.; Maartman-Moe, M.; Maroy, K. *Acta Chem. Scand.* 1986, A40, 685.
- (24) Elder, R. C.; Marcuso, T.; Boorschand, P. *Inorg. Chem.* 1977, 16, 2700.
- (25) Ault, H. K.; Husebye, S. *Acta Chem. Scand.* 1978, A32, 157.
- (26) Rout, G. C.; Seshasayee, M.; Aravamudan, G.; Sowrirajan, S. *Polyhedron* 1984, 3, 921.
- (27) Rout, G. C.; Seshasayee, M.; Aravamudan, G.; Sowrirajan, S. *J. Crystallogr. Spectrosc. Res.* 1985, 15, 377.
- (28) Anderson, O. P. *Acta Chem. Scand.* 1971, 25, 3593.
- (29) Rout, G. C.; Seshasayee, M.; Aravamudan, G.; Sowrirajan, S. *Acta Chem. Scand.* 1984, C40, 963.
- (30) Foss, O.; Maroy, K.; Husebye, S. *Acta Chem. Scand.* 1965, 19, 2361.
- (31) Ase, K.; Roti, I. *Acta Chem. Scand.* 1974, A28, 104.
- (32) Ase, K.; Boyum, K.; Foss, O.; Maroy, K. *Acta Chem. Scand.* 1971, 25, 2457.
- (33) Foss, O.; Lyssandtrae, N.; Maartmann-Moe, K.; Tysseland, M. *Acta Chem. Scand.* 1973, 27, 218.
- (34) Ase, K.; Maartmann-Moe, K.; Solheim, J. O. *Acta Chem. Scand.* 1971, 25, 2467.
- (35) Ase, K. *Acta Chem. Scand.* 1969, 23, 3206.
- (36) Foss, O.; Henjum, J.; Maartmann-Moe, K.; Maroy, K. *Acta Chem. Scand.* 1987, A41, 77.
- (37) Beno, M. A.; Sundell, R.; Williams, J. M. *Croat. Chim. Acta* 1984, 57, 695.
- (38) Foss, O.; Hauge, S. *Acta Chem. Scand.* 1965, 19, 2395.
- (39) Foust, A. S. *Inorg. Chem.* 1980, 19, 1050.
- (40) Foss, O.; Johnsen, K.; Maartmann-Moe, K.; Maroy, K. *Acta Chem. Scand.* 1966, 20, 113.
- (41) Foss, O.; Maartmann-Moe, K. *Acta Chem. Scand.* 1987, A41, 121.
- (42) Fredin, K. S.; Maroy, K.; Slogvik, S. *Acta Chem. Scand.* 1975, A29, 212.
- (43) Foss, O.; Maartmann-Moe, K. *Acta Chem. Scand.* 1986, A40, 675.
- (44) Ase, K.; Foss, O.; Roti, I. *Acta Chem. Scand.* 1971, 25, 3808.
- (45) Foss, O.; Kjøge, H. M.; Maroy, K. *Acta Chem. Scand.* 1965, 19, 2349.
- (46) Herland, P.; Lundeland, W.; Maroy, K. *Acta Chem. Scand.* 1976, A30, 719.
- (47) Foss, O.; Johannessen, W. *Acta Chem. Scand.* 1961, 15, 1940.
- (48) Eide, J.; Foss, O.; Maartmann-Moe, K.; Maberg, O.; Scheie, A. *Acta Chem. Scand.* 1987, A41, 67.
- (49) Foss, O.; Maroy, K. *Acta Chem. Scand.* 1986, A40, 669.
- (50) Foss, O.; Maroy, K. *Acta Chem. Scand.* 1966, 20, 123.
- (51) Hauge, S.; Vikane, O. *Acta Chem. Scand.* 1975, A29, 755.
- (52) Foss, O.; Husebye, K.; Maroy, K. *Acta Chem. Scand.* 1963, 17, 1806.
- (53) Hauge, S.; Johannessen, O.; Vikane, O. *Acta Chem. Scand.* 1978, A32, 901.
- (54) Husebye, S.; Maartmann-Moe, K.; Mikalsen, O. *Acta Chem. Scand.* 1990, 44, 464.
- (55) Foss, O.; Husebye, S. *Acta Chem. Scand.* 1966, 20, 132.
- (56) Vikane, O. *Acta Chem. Scand.* 1975, A29, 763.
- (57) Vikane, O. *Acta Chem. Scand.* 1975, A29, 738.
- (58) Vikane, O. *Acta Chem. Scand.* 1975, A29, 787.
- (59) Hauge, S.; Vikane, O. *Acta Chem. Scand.* 1985, A39, 553.
- (60) Foss, O.; Larssen, P. A. *Acta Chem. Scand.* 1954, 8, 1042.
- (61) Maroy, K. *Acta Chem. Scand.* 1971, 25, 2557.
- (62) Maroy, K. *Acta Chem. Scand.* 1973, 27, 1695.
- (63) Gjerrestad, K.; Maroy, K. *Acta Chem. Scand.* 1973, 27, 1653.
- (64) Foss, O.; Vihovde, E. H. *Acta Chem. Scand.* 1954, 8, 1032.
- (65) Ase, K. *Acta Chem. Scand.* 1971, 25, 838.
- (66) Oyum, P.; Foss, O. *Acta Chem. Scand.* 1955, 9, 1012.
- (67) Foss, O.; Oyum, P. *Acta Chem. Scand.* 1955, 9, 1014.

- (68) Husebye, S.; Maartmann-Moe, K.; Mikalsen, O. *Acta Chem. Scand.* 1989, 43, 963.
- (69) Esperas, S.; Husebye, S.; Svaeren, S. E. *Acta Chem. Scand.* 1971, 25, 3539.
- (70) Husebye, S.; Svaeren, S. E. *Acta Chem. Scand.* 1973, 27, 763.
- (71) Kumar, V.; Aravamudan, G.; Seshasayee, M.; Selvam, P.; Yvon, K. *Acta Crystallogr.* 1990, C46, 2100.
- (72) Husebye, S. *Acta Chem. Scand.* 1979, A33, 485.
- (73) Rout, G. C.; Seshasayee, M.; Aravamudan, G.; Radha, K. *Acta Crystallogr.* 1984, C40, 1142.
- (74) Esperas, S.; Husebye, S. *Acta Chem. Scand.* 1973, 27, 706.
- (75) Esperas, S.; Husebye, S. *Acta Chem. Scand.* 1975, A29, 185.
- (76) Chidambaram, S.; Aravamudan, G.; Seshasayee, M.; Shibanova, T. A.; Simonov, V. I. *Polyhedron* 1988, 7, 1267.
- (77) Rout, G. C.; Seshasayee, M.; Aravamudan, G.; Radha, K. *J. Crystallogr. Spectrosc. Res.* 1984, 14, 193.
- (78) Husebye, S.; Thowsen, A. *Acta Chem. Scand.* 1981, A35, 386.
- (79) Von Deuten, K.; Schnabel, W.; Klar, G. *Phosphorus Sulfur* 1980, 9, 93.
- (80) Appa Rao, G. V. N.; Seshasayee, M.; Aravamudan, G.; Radha, K. *Inorg. Chem.* 1983, 22, 2590.
- (81) Husebye, S.; Thowsen, A. G. *Acta Chem. Scand.* 1981, A35, 443.
- (82) Chidambaram, S.; Aravamudan, G.; Seshasayee, M.; Snow, M. C.; Tiekink, E. R. T. *Aust. J. Chem.* 1989, 42, 969.
- (83) Esperas, S.; Husebye, S. *Acta Chem. Scand.* 1972, 26, 3293.
- (84) Dakternieks, D.; Di Giacomo, R.; Gable, R. W.; Hoskins, B. F. *J. Am. Chem. Soc.* 1988, 110, 6762.
- (85) Husebye, S.; Maartmann-Moe, K.; Steffensen, W. *Acta Chem. Scand.* 1990, 44, 579.
- (86) Appa Rao, G. V. N.; Seshasayee, M.; Aravamudan, G.; Radha, K. *Acta Crystallogr.* 1983, C39, 1018.
- (87) Kumar, V.; Aravamudan, G.; Seshasayee, M. *J. Crystallogr. Spectrosc. Res.* 1991, 21, 65.
- (88) Schnabel, W.; Von Deuten, K.; Klar, G. *Cryst. Struct. Commun.* 1981, 13, 345.
- (89) Schnabel, W.; Von Deuten, K.; Klar, G. *Phosphorus Sulfur* 1982, 13, 345.
- (90) Bailey, J. H. E.; Drake, J. E. *Can. J. Chem.* 1993, 71, 42.
- (91) Bailey, J. H. E.; Drake, J. E.; Sarkar, A. B.; Wong, M. L. H. *Can. J. Chem.* 1989, 67, 1735.
- (92) Alcock, N. W.; Culver, J.; Roe, S. M. *J. Chem. Soc. Dalton Trans.* 1992, 1477.
- (93) Chadha, R. K.; Drake, J. E.; McManus, N. T.; Quinlan, B. A.; Sarkar, A. B. *Organometallics* 1987, 6, 813.
- (94) Dakternieks, D.; Di Giacomo, R.; Gable, R. W.; Hoskins, B. F. *J. Organometal. Chem.* 1988, 349, 305.
- (95) Bogason, J. O.; Dakternieks, D.; Husebye, S.; Maartmann-Moe, K.; Zhu, H. *Phosphorus, Sulfur, Silicon* 1992, 71, 13.
- (96) Dakternieks, D.; Di Giacomo, R.; Gable, R. W.; Hoskins, B. F. *J. Am. Chem. Soc.* 1988, 110, 6753.
- (97) Dakternieks, D.; Di Giacomo, R.; Gable, R. W.; Hoskins, B. F. *J. Organometal. Chem.* 1988, 353, 35.
- (98) Bailey, J. H. E.; Drake, J. E.; Wong, M. L. Y. *Can. J. Chem.* 1991, 69, 1948.
- (99) Von Deuten, K.; Schnabel, W.; Klar, G. *Cryst. Struct. Commun.* 1980, 9, 161.
- (100) Weiss, J.; Pupp, M. *Acta Crystallogr.* 1972, B28, 3653.
- (101) Hoskins, B. F.; Pannan, C. D. *J. Chem. Soc., Chem. Commun.* 1975, 408.
- (102) Hoskins, B. F.; Pannan, C. D. *Aust. J. Chem.* 1976, 29, 2337.
- (103) Hoskins, B. F.; Oliver, P. J.; Winter, G. *Inorg. Chim. Acta* 1984, 86, L21.
- (104) Hoskins, B. F.; Tiekink, E. R. T.; Winter, G. *Inorg. Chim. Acta* 1985, 96, L79.
- (105) Hummel, H. U.; Fischer, T.; Moll, M.; Wolski, A. *Z. Naturforsch.* 1992, 47b, 344.
- (106) Bjornevag, S.; Husebye, S.; Maartmann-Moe, K. *Acta Crystallogr.* 1981, A37 Suppl., C-240.
- (107) Bjornevag, S.; Husebye, S.; Maartmann-Moe, K. *Acta Chem. Scand.* 1982, A36, 195.
- (108) Husebye, S.; Maartmann-Moe, K.; Mikalsen, O. *Acta Chem. Scand.* 1990, 44, 802.
- (109) Huang, S. P.; Dhingra, S.; Kanatzidis, M. G. *Polyhedron* 1992, 11, 1869.
- (110) Golic, L.; Dietsch, W.; Köhler, K.; Stach, J.; Kirmse, R. *J. Chem. Soc., Dalton Trans.* 1988, 97.
- (111) Gable, R. W.; Hoskins, B. F.; Steen, R. J.; Winter, G. *Inorg. Chim. Acta* 1982, 65, L127.
- (112) Gable, R. W.; Hoskins, B. F.; Steen, R. J.; Winter, G. *Inorg. Chim. Acta* 1983, 72, 173.
- (113) Subramanyam, T.; Avaramudan, G.; Rout, G. C.; Seshasayee, M. *J. Crystallogr. Spectrosc. Res.* 1984, 14, 239.
- (114) Ahmed, M. A. K.; McCarthy, A. E.; McWhinnie, W. R.; Berry, F. *J. Chem. Soc., Dalton Trans.* 1986, 771.
- (115) West, A. A.; McWhinnie, W. R.; Hamor, T. A. *J. Organometal. Chem.* 1988, 356, 159.
- (116) Ahmed, M. A. K.; McWhinnie, W. R.; Hamor, T. A. *J. Organometal. Chem.* 1985, 293, 219.
- (117) Al-Salim, N.; West, A. A.; McWhinnie, W. R.; Hamor, T. A. *J. Chem. Soc., Dalton Trans.* 1988, 2363.
- (118) Newton, M. G.; King, R. B.; Haiduc, I.; Silvestru, A. *Inorg. Chem.* 1993, 32, 3795.
- (119) Ganesh, V.; Seshasayee, M.; Kumar, V.; Chidambaram, S.; Aravamudan, G.; Goubitz, K.; Schenk, H. *J. Crystallogr. Spectrosc. Res.* 1989, 19, 745.
- (120) Dakternieks, D.; Di Giacomo, R.; Gable, R. W.; Hoskins, B. F. *J. Am. Chem. Soc.* 1988, 110, 6541.
- (121) Wieber, M.; Schmidt, E.; Burschka, C. Z. *Anorg. Allgem. Chem.* 1985, 525, 127.
- (122) Husebye, S.; Maartmann-Moe, K.; Steffensen, W. *Acta Chem. Scand.* 1990, 44, 139.
- (123) Drake, J. E.; Wong, M. L. Y. *N. J. Organomet. Chem.* 1989, 377, 43.
- (124) Singh, A. K.; Basumatary, J. K.; Singh, T. P.; Padmanabhan, B. *J. Organomet. Chem.* 1992, 424, 33.
- (125) Lee, J. S.; Titus, D. D.; Ziolo, R. F. *J. Chem. Soc., Chem. Commun.* 1976, 501.
- (126) Lee, J. S.; Titus, D. D.; Ziolo, R. F. *Inorg. Chem.* 1977, 16, 2487.
- (127) Brondmo, N. J.; Esperas, S.; Graver, H.; Husebye, S. *Acta Chem. Scand.* 1973, 27, 713.
- (128) Graver, H.; Husebye, S. *Acta Chem. Scand.* 1975, A29, 14.
- (129) Tiekink, E. R. T. *Acta Crystallogr.* 1986, C42, 633.
- (130) Husebye, S. *Acta Chem. Scand.* 1967, 21, 42.
- (131) Hoskins, B. F.; Tiekink, E. R. T.; Winter, G. *Inorg. Chim. Acta* 1985, 105, 171.
- (132) Fabiani, C.; Spagna, R.; Vaciago, A.; Zambonelli, L. *Acta Crystallogr.* 1971, B27, 1499.
- (133) Ganesh, V.; Seshasayee, M.; Chidambaram, S.; Aravamudan, G.; Goubitz, K.; Schank, H. *Acta Crystallogr.* 1989, C45, 1506.
- (134) Kumar, V.; Aravamudan, G.; Seshasayee, M.; Selvam, P.; Yvon, K. *Acta Crystallogr.* 1990, C46, 2081.
- (135) Husebye, S. *Acta Chem. Scand.* 1970, 24, 2198.
- (136) Rout, G. C.; Seshasayee, M.; Radha, K.; Aravamudan, G. *Acta Crystallogr.* 1983, C39, 1021.
- (137) Radha, K.; Aravamudan, G.; Rajalakshmi, A.; Rout, G. C.; Seshasayee, M. *Aust. J. Chem.* 1986, 39, 847.
- (138) Husebye, S. *Acta Chem. Scand.* 1966, 20, 24.
- (139) Refaat, L. S.; Maartmann-Moe, K.; Husebye, S. *Acta Chem. Scand.* 1984, A38, 147.
- (140) Husebye, S.; Maartmann-Moe, K.; Mikalsen, O. *Acta Chem. Scand.* 1989, 43, 754.
- (141) Husebye, S.; Maartmann-Moe, K.; Mikalsen, O. *Acta Chem. Scand.* 1989, 43, 868.
- (142) Silvestru, A.; Haiduc, I.; Ebert, K. H.; Breunig, H. J. Submitted for publication.
- (143) Gerl, H.; Eisenmann, B.; Roth, H.; Schafer, H. *Z. Anorg. Allgem. Chem.* 1974, 407, 135.
- (144) Jumas, J. C.; Ribes, M.; Maurin, M.; Philippon, E. *Acta Crystallogr.* 1976, B32, 444.
- (145) McCarthy, J. J.; Zhang, X.; Kanatzidis, M. *Inorg. Chem.* 1993, 32, 2944.
- (146) Wynne, K. J. *J. Chem. Educ.* 1973, 50, 328.
- (147) Hoskins, B. F.; Pannan, C. D. *Aust. J. Chem.* 1976, 29, 2541.
- (148) Bailey, J. E.; Drake, J. E. *Can. J. Chem.* 1993, 71, 42.
- (149) Krishna Kumar, R.; Aravamudan, G.; Udupa, M. R.; Seshasayee, M.; Hamor, T. A. *Polyhedron* 1993, 12, 2201.