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DEVELOPMENTS IN CHALCOGEN–HALIDE CHEMISTRY

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I. Introduction

The chemistry and structural chemistry of the chlorides, bromides, and iodides of sulfur, selenium, and tellurium (i.e., of the "chalcogens") has been the subject of intensive preparative efforts and of various investigations into their structural and bonding properties and has developed into a fascinating field of main group chemistry within the last two decades. This is especially valid for the chalcogen(+IV) and chalcogen(+II) species with s^2 or s^2p^2 ground state configuration of the central sulfur, selenium, or tellurium atoms, the stereochemistry (and within certain limits, the reactivity) of which is determined to a large extent by the strongly variable stereochemical activity of the inert electron pairs in the valence shell of the chalcogen. In the solid and liquid state, the structural nature of these subvalent compounds cannot be readily predicted and described using simple models as for free molecules in the gas phase (e.g., the VSEPR model); it is rather determined by secondary effects such as maximization of Coulomb forces by ion formation, by association effects of various kinds, and by varying polarizing effects of the ligands. Although these properties result in a rich and variable structural chemistry, it is evident that there is no comprehensive concept for the prediction and understanding of bonding and structure of those systems. Current bonding descriptions that are being discussed frequently are based partly on molecular orbital and partly on valence bond models, and they use, e.g., the concepts of the simple VSEPR model (*152–155*) or of hypervalence (*324*), different variants of multicenter bonding (392), charge transfer interactions, or the distinction of primary and secondary bonding (*24, 323*) in the coordination sphere of the chalcogen atoms (see also *399*).

In the literature, there is a lack of specific recent review articles on the compounds of sulfur, selenium, and tellurium with the heavy halogens [exceptions are, e.g., reports on sulfur compounds (*117, 176, 277, 386*) and on the subhalides of tellurium (*237*)], although this whole area is an important field of large current interest (for general accounts in more comprehensive monographs and reference works, see *31, 32, 83, 158–162, 244, 291, 449*).

In the following, an account of some recent preparative and structural aspects of the field within the last years will be given. The chapter will be selective rather than comprehensive and will concentrate primarily on the inorganic chemistry of the binary chlorides, bromides, and iodides as well as on the corresponding hypervalent anionic and cationic halo derivatives; fluorides (see, e.g., *104*) are referred to in only a few cases; no extensive coverage of organo derivatives of the chalcogen halides or of the various branches of the chemistry of sulfenyl, thionyl, and sulfuryl halides, including their technical relevance in organic synthesis, is given. One intention of the chapter is to demonstrate how the variability of the structural and bonding properties of the "inert pair" systems of the chalcogens in their formally lower positive oxidation states influences directly the reactivity and the nature of the variety of possible reaction products. In this sense, this field of chemistry may serve as a model for bonding, structure and reactive properties of analogous s^2 systems of neighboring elements such as Sb(III), Bi(III), or I(V). Recent investigations (e.g., on antimony(III) and arsenic(III) halogen compounds have indicated quite similar structural principles as in Te(IV) analogues (*366–370, 410*, and literature cited in *399*).

II. Chalcogen(IV) Compounds

A. Binary Halides

In the series of the binary halides of selenium and tellurium, the crystal structure determinations of tellurium tetrafluoride (*100*) and of tellurium tetrachloride on twinned crystals (*65, 66*) were the key to understanding the various and partly contradictory spectroscopic and other macroscopic properties (e.g., *66, 161, 168, 169, 219, 220, 412*), as well as the synthetic potential of the compounds. In contrast to the monomeric molecular ψ-tbp gas phase structures with C_{2v} symmetry (*417*), the solid state structures of both are polynuclear. As the prototype of the chlorides and bromides of selenium and tellurium, crystalline tellurium(IV) chloride has a cubane-like tetrameric structure with approximate T_d symmetry (Fig. 1). Within the distorted $TeCl_{3+3}$ octahedra the bonds to the triply bridging chlorine ligands are much longer than to the terminal chlorines. The bonding system can be described either covalently as Te_4Cl_{16} molecules, or, in an ionic approximation, as $[(TeCl_3^+Cl^-)_4]$ with a certain degree of stereochemical activity of the lone pairs toward the center of the voluminous cubane center (*65, 66*).

In the tellurium(IV) fluoride structure with chains of corner-sharing TeF_5 tetragonal pyramids (*100*), the lone pair (*E*) is stereochemically much more active and occupies one position in the ψ-octahedral TeF_5E polyhedra, in accordance with simple VSEPR considerations (Fig. 2).

Interestingly, a second tetrameric structure type is observed in the thermodynamically stable ∂-modification (see below) of tellurium(IV) iodide in which significantly less-distorted octahedra are linked in a different way, containing doubly bridging halogen atoms in addition to triply bridging ones (see Fig. 2). It appears that this structural type favors more symmetrical coordination polyhedra with less polar bonds. The ionic formulations $[(TeCl_3^+Cl^-)_4]$ and $[(TeI_3^+I^-)_2(TeI_4)_2]$ of the two molecular types indicate a larger charge separation in the tellurium–halogen bonds in the cubane-like structure, in accordance with the trend in the electronegativity differences.

Figure 2 shows all three basic structure types of the solid chalcogen(IV) halides. Three characteristic structural and bonding features of the halogen compounds of the chalcogen(IV) systems, in which the role

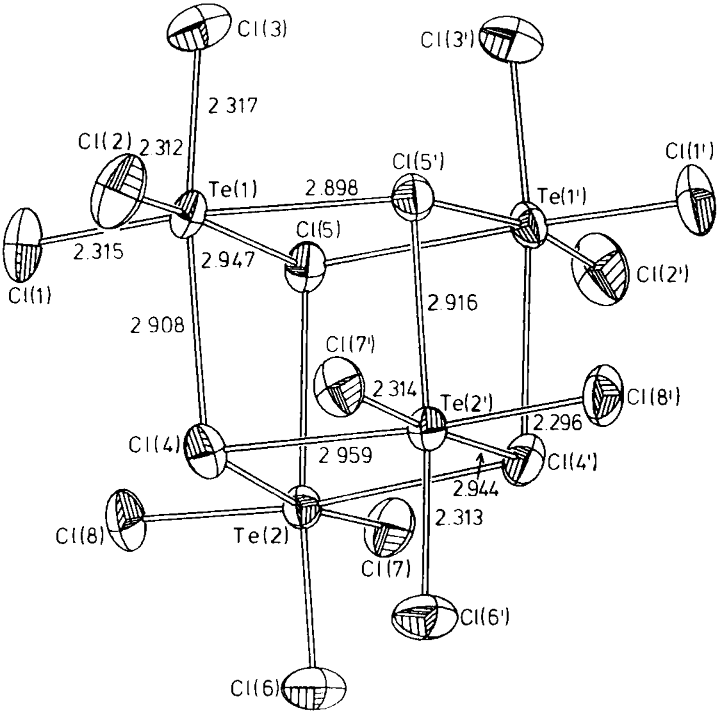


FIG. 1. Molecular structure of tellurium(IV) chloride in the crystal, with bond lengths (Å) (*65*).

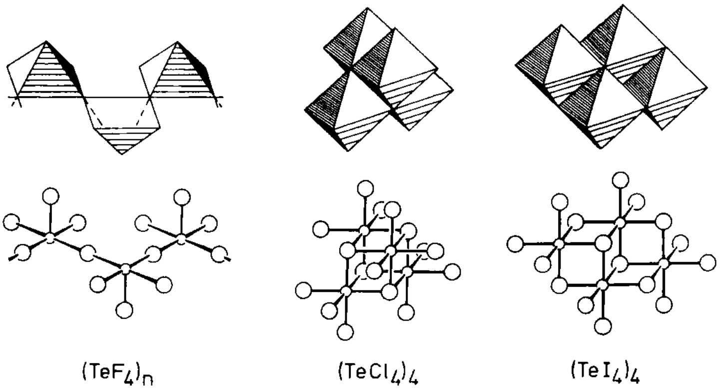


FIG. 2. Comparison of the molecular structures of the tellurium(IV) fluoride, chloride, and iodide types in the solid state. The selenium(IV) chlorides and bromides as well as tellurium(IV) bromide and one of the five forms of tellurium(IV) iodide are isostructural to the cubane-like Te_4Cl_{16} molecules (*244*).

of the inert pair determines much of the stereochemistry and reactive properties of the whole class of compounds, are evident already in the simple binary halides:

1. Sulfur(IV), selenium(IV), and tellurium(IV) try to form a more or less distorted quasi-octahedral $XY_{3+3}E$ or $XY_{4+2}E$ coordination of six nearest neighbors in which there is a tendency to form stable trigonal-pyramidal XY_3^+ sub-units (X is S, Se, Te; Y is Cl, Br, I; E is a more or less stereochemically active electron pair).
2. The harder [in Pearson's model (*365*)] or the more electronegative the ligand is, the more pronounced is the stereochemical activity of the inert electron pair at the chalcogen. Fluorine has an especially strong "trans-directing" influence on the inert pair and activates it stereochemically, as shown, for example, in the structures of TeF_4 (Fig. 2) or of TeF_5^- in $KTeF_5$ (*101, 284*). A similar tendency is observed for oxygen as ligand atom and, interestingly, for organo ligands in organo-chalcogen-halogen compounds (see later, Fig. 8).
3. A similar trend is observed as a function of the central chalcogen atoms: in the series from sulfur (electronegative and hard) to selenium and tellurium (less electronegative and softer) as central atoms, the symmetry of the XY_n polyhedra in the solid compounds increases (i.e., the stereochemical activity of the inert pairs decreases) and the tendency to form ionic substructures such as XY_3^+ is greatly reduced.

More examples for these trends, which have been discussed somewhat more generally (*222, 438*), will be shown in the following.

Significant progress has been reported in the last years on all the known chalcogen(IV) halides; in their structure and bonding they all are related to the three prototype molecular structures referred to above. Results in detail are reviewed here.

1. Sulfur Halides

SCl_4, as the only stable tetrahalide of sulfur besides SF_4, is known to be easily prepared at temperatures below −34°C from the elements or from the reversible reaction of equimolar amounts of SCl_2 and chlorine. Recent investigations of the system S/Cl by low-temperature thermoanalytic methods (*233, 330*) show congruent melting of SCl_4 at −34°C and, besides the known compounds SCl_2 and S_2Cl_2, a hitherto unknown compound of composition SCl_3 (*233*) with an incongruent melting point of −75°C and with a proposed constitution of a 1 : 1 adduct of SCl_2 with SCl_4. In the more chlorine-rich region, Cl_3^- ions are very probably formed, and from spectroscopic evidence the existence of a compound $SCl_3^+Cl_3^-$ can be proposed (*115*).

No single crystals of SCl_4 could be obtained yet, and the full structure is unknown. According to X-ray powder diagrams at −90°C it is proposed to be isotypic to cubic α-$SeCl_4$ (see below) with tetrameric $[(SCl_3{}^+Cl^-)_4]$ molecules (*233*). The presence of trigonal pyramidal SCl_3^+ units in the structure is evident from vibrational frequencies of 472 and 450 cm^{-1} observed in the Raman and infrared spectra (*115, 416*), to be assigned to the stretching vibrations of the trigonal pyramidal species. The association of the SCl_3^+ groups through Cl^- is indicated from the significant lowering of these frequencies as compared to the isoelectronic, largely molecular PCl_3. The large differences of the vibrational spectra of SCl_4 if compared to those of α-$SeCl_4$ (*56, 192, 373*) are, however, put forward against an isotypic relation between both (*416*). A single-crystal structure analysis on SCl_4 is desirable.

Matrix isolation experiments were successful to prepare the mixed-ligand sulfurane molecules SCl_3F, SCl_2F_2, and $SClF_3$ and to characterize them by their vibrational spectra. They are formed in the gas phase via co-condensation of SCl_2 with ClF or F_2. SCl_2F_2 is the most stable species in this series, and the vibrational spectrum and a normal coordinate analysis suggest a C_{2v} structure, as for SF_4 (*311*). Sublimation of $[CF_3SCl_2^+][AsF_6^-]$ and trapping of AsF_5 as $KAsF_6$ has led to the very unstable mixed-ligand sulfurane CF_3SCl_2F, which was isolated at low temperatures and characterized by vibrational and ^{19}F NMR spectra (*308*). $CF_3S{-}SCl_2^+Cl^-$, as the trifluoromethyl derivative of SCl_4 ($SCl_3^+Cl^-$), was prepared recently by reaction of CF_3SSCl with Cl_2 at low temperatures. It is a yellow solid that behaves very similarly to SCl_4 itself and decomposes reversibly back to the starting materials at temperatures above −40°C; it was identified from its Raman spectrum at −196°C (*315*).

2. *Selenium Halides*

As recent thermoanalytical and X-ray diffraction investigations show, $SeCl_4$ can be prepared in two polymorphic modifications, a metastable β-form (*52, 192, 230*) and a thermodynamically stable α-modification (*164, 231*). β-$SeCl_4$ is obtained (a) by crystallization from solvents such as $POCl_3$; (b) by sublimation of gaseous $SeCl_4$ (which contains also $SeCl_2$ and Cl_2 as dissociation products) into a zone with $T < 150°C$; and (c) by crystallization from the melt (mp 306°C). α-$SeCl_4$ is formed (a) in the solid by monotropic transformation above 180°C, and (b) during the sublimation if, at deposition temperatures above 210°C, the primary product β-$SeCl_4$ is transformed to the stable phase according to the Ostwald rule. The structure of β-$SeCl_4$ is an isotype to $TeCl_4$ and contains tetrameric cubane-like Se_4Cl_{16} molecules with approximate T_d symmetry (exact point symmetry C_2). The structure of the stable α-phase is cubic. It also contains the cubane-like tetramers with very similar geometrical details that are, however, on two different crystallographic sites with S_4 and T symmetries, and in positions that correspond to those of the atoms of the β-tungsten structure type.

It is known that $SeBr_4$, when freshly prepared from the elements, changes from red to black after some time. Phase investigations in the system Se–Br show two modifications of $SeBr_4$ (mp +5°C), a thermodynamically stable black α-modification and a red β-form, and also show that the change in color is due to the irreversible phase transformation from the α- to the initially formed β-modification (*51;* see also *164*). Both crystalline forms of selenium tetrabromide contain cubane-like tetrameric molecules of the Te_4Cl_{16} type. Monoclinic β-$SeBr_4$ is an isotype to the $TeCl_4$ structure (*65, 66*), whereas a different kind of packing of the Se_4Br_{16} molecules is observed in trigonal α-$SeBr_4$. As in the $SeCl_4$ structures, the relative difference of the terminal and bridging Se–Br(Cl) bond lengths (*51*) is larger than in the tellurium analogues (*65–67, 246*), indicating a closer approximation to the ionic limiting structures $[(XY_3^+Y^-)_4]$ than in tellurium tetrachloride and bromide. Strangely, the density of α-$SeBr_4$ is much lower than the one of β-$SeBr_4$ (d_x 3.87 vs. 4.34 gcm^{-3}).

It has not yet been possible to prepare SeI_4.

3. *Tellurium Halides*

Besides TeF_4 and $TeCl_4$, the tetrabromide and the tetraiodide were also characterized structurally. The crystal structure of $TeBr_4$ is an isotype to $TeCl_4$ (*67, 244, 246*) with the same twinning principle and with similar shape and bonding of the cubane-like molecules.

An unusually large number of five different polymorphic modifications were identified for TeI_4 (*228, 40*). Crystals are obtained from solutions of TeI_4 and concentrated HI in methanol. According to thermoanalytical studies, ∂-TeI_4 (the phase described above, *257, 363*) is the only thermodynamically stable one at normal conditions. The stability of the other four modifications increases in the sequence ϵ-, γ-, β-, and α-TeI_4; phase transformations to the final phase ∂-TeI_4 are possible by heating up to the melting point of 280°C, and they run through discrete intermediates. Trigonal α-TeI_4 is an isotype of the 2H–CdI_2 structure with a probable random distribution of Te over the Cd positions, the molecular connectivity within the structure being unknown. Orthorhombic β-TeI_4 and monoclinic γ-TeI_4 contain the tetrameric $[(TeI_3{}^+I^-)_2(TeI_4)_2]$ molecules as observed in ∂-TeI_4 with ordered distributions of Te over one-fourth of the octahedral voids of a 2H- (β) and a

4H-sequence (γ, ∂) of the nearly close-packed iodine layers. In Fig. 3 the structures of the Te_4I_{16} molecules in the ∂- and γ-modifications is shown. The least stable tetragonal ε-TeI_4 is the only form that contains cubane-like $[(TeI_3^+I^-)_4]$ molecules (Fig. 1 and 2) as observed in the $TeCl_4$ and $TeBr_4$ structures, however in a different intermolecular arrangement with nearly cubic close packing of the iodine atoms (*40*, *228*). Crystallographic data on the TeI_4 modifications are given in Table I, together with the known unit cells and space groups of the other binary chalcogen(IV) halides.

A large number of investigations have been reported on spectroscopic, thermodynamic, and other equilibrium properties of chalcogen tetrahalides (e.g., *158–162*). They include vibrational spectroscopic analyses of $SeCl_4$ and $TeCl_4$ in the solid on the basis of the known structures (*89*, *373*) and in the gas phase (*37*), equilibrium measurements of $SeCl_4$ and $TeCl_4$ in molten salts (*112*, *376*, *422*), determination of enthalpies of formation (*335*, *339*, *433*), other equilibrium studies, and determination of thermodynamic data from vapor pressure measurements, mass spectrometric investigations, conductivity experiments, and thermal phase analysis in the solid (*37*, *39*, *203*, *275*, *333*, *337*, *339*, *340*, *341*, *342*, *379*, *402*, *403*).

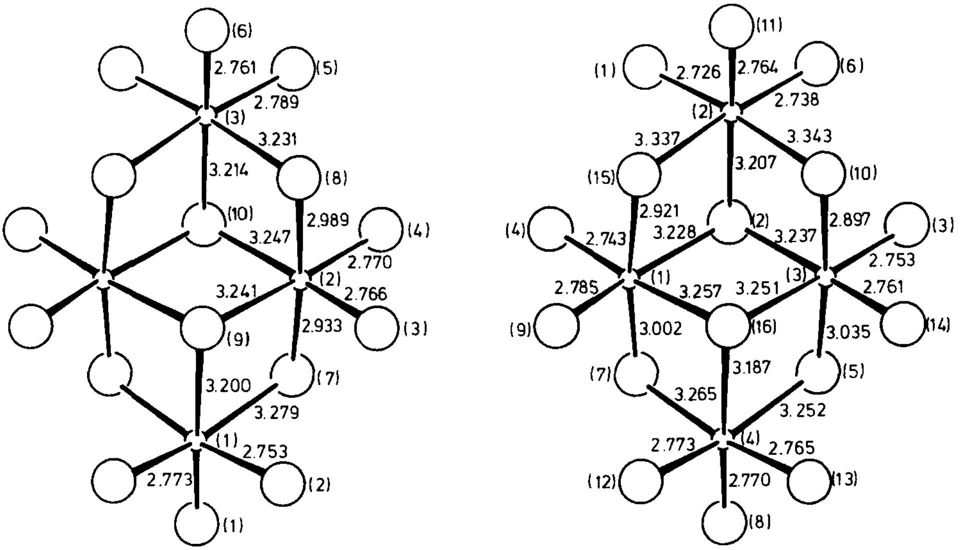


FIG. 3. Tetrameric molecules in the crystal structures of ∂-TeI_4 (left) and γ-TeI_4 (right) with bond lengths (Å) (*228*, *363*).

TABLE I

CRYSTALDATA OF CHALCOGEN TETRAHALIDES

Formula	Cell constants (293 K)				Space group	Reference
	a (Å)	b (Å)	c (Å)	β(°)		
Scl$_4$^{a}	15.80(4)				Cubic	*233*
α-SeCl$_4$	16.433				$P\bar{4}3n$	*231*
β-SeCl$_4$	16.548(1)	9.810(1)	15.029(1)	116.95(1)	C2/c	*52*
α-SeBr$_4$	10.200(7)		30.35(2)		P31c	*51*
β-SeBr$_4$	17.02	10.39	15.49	117.0	C2/c	*51*
TeCl$_4$	17.076(8)	10.404(5)	15.252(8)	116.82(5)	C2/c	*66*
TeBr$_4$	17.803(7)	10.882(3)	15.947(5)	116.77(3)	C2/c	*67*
α-TeI$_4$	4.228(2)		6.684(6)		$P\bar{3}m1$	*228*
β-TeI$_4$	6.888(2)	14.539(3)	16.753(4)		Pn2_1m	*228*
γ-TeI$_4$	11.199(4)	13.599(4)	22.158(6)	98.10(3)	P2_1/c	*228*
∂-TeI$_4$	13.635(5)	16.798	14.624(5)		Pnma	*363*
ϵ-TeI$_4$	16.875(6)		11.829(5)		I4_1/amd	*228*

[a] 183 K.

[b] (α-ε teI$_4$); see also *40*.

It is important to note that the tetrahalides of selenium and tellurium evaporate as monomeric XY_4 or ($XY_2Y'_2$) molecules (X = Se, Y = Cl, Br; X = Te, Y = Cl, Br, I) but that they are in equilibrium with the corresponding dihalides (see Section III,A) as dissociation products (*158, 160–162, 275, 298, 334, 335, 337, 339, 340, 341, 344, 447*):

$$XY_4(g,s) \rightarrow XY_2(g) + Y_2(g) \tag{1}$$

For TeI$_4$ a second dissociation reaction

$$TeI_4(g) \rightarrow Te(s) + 2I_2(g) \tag{2}$$

takes place besides the first one (*339, 341*). These equilibria have been investigated by vapor pressure, spectroscopic, mass spectrometric, and thermoanalytic measurements (see Section III,A). As shown by these studies, the dissociation equilibria, together with additional equilibria involving gaseous $TeOCl_2$ and $TeOBr_2$, are the basis for the remarkable role of the tellurium tetrahalides (thermodynamic data: *337, 339*) in chemical transport reactions (*403*). $TeCl_4$ and $TeBr_4$, in equilibrium with their reaction products $TeCl_2$ ($TeBr_2$), Cl_2 (Br_2), $TeOCl_2$ ($TeOBr_2$), or with HCl (HBr), are excellent systems for chemical transport, purification, and crystal production of a variety of metal oxides (e.g., *150, 151, 343, 402;* see Section II,E). The $TeI_4/TeI_2/Te$ system can be employed for the transport and purification of elemental tellurium (*63, 339, 341*).

4. *Mixed-Ligand Halides*

As novel halides-pseudohalides of a tetravalent chalcogen, tellurium trichloride azide, Cl_3TeN_3, and tellurium dichloride diazide, $Cl_2Te(N_3)_2$, were prepared from CH_2Cl_2 solutions of $TeCl_4$ and trimethylsilyl azide according to

$$n(CH_3)_3SiN_3 + TeCl_4 \xrightarrow{n\,=\,1,2} Cl_{4-n}Te(N_3)_n + n(CH_3)_3SiCl \qquad (3)$$

and were characterized by their IR spectra (*434*). The most probable structure of Cl_3TeN_3 is a dimer similar to $(SeOCl_3)_2$ (Fig. 23 shown later). $TeBr_4$ does not react with trimethylsilyl azide; SCl_4 and $SeCl_4$ do react, however, toward SCl_2 or "SeCl" together with dinitrogen as stable products. The trichloride azides and the nitrides Cl_3XN are assumed to be unstable intermediates. Also, the mixed halides-pseudohalides $(CF_3)_2TeCl_2$ and $(CF_3)_2TeBr_2$ were obtained by reactions of $(CF_3)_2Te$ with Cl_2 or Br_2; at higher halogen concentrations CF_3TeCl_3 and CF_3TeBr_3 were produced (*194*). The bis(trifluoromethyl)tellurium dihalides can be used as reagents for different types of exchange reactions, for example, with acid anhydrides (*195*).

Two other interesting derivatives of tellurium tetrahalides, Cl_2TeS_7 and Br_2TeS_7, (which might as well be classified as heteroatomic chalcogen subhalides—see Section IV) were prepared from the reactions of $TeCl_4$ or $TeBr_4$ with crude sulfane mixtures (*430, 431*). The molecular structures contain a heteronuclear eight-membered TeS_7 ring and derive from cyclo-octasulfur by replacement of one S by a TeY_2 group ($Y = Cl, Br$). The conformation of the ring remains very similar to that of the S_8 ring. In the ψ-trigonal bipyramidal coordination around Te, the two halogen ligands are trans to each other, the Te–Y bond axial to the ring being much shorter than the equatorial one (Cl_2TeS_7: 2.400 vs. 2.536 Å) (*430, 431*). The Cl_2TeS_7 molecule is shown in Fig. 4.

Some remarkable N-substituted derivatives of $SeCl_4$ with significant Se–N multiple bonding have been obtained from the reaction of $(C_6H_5)_3P{-}N{-}Si(CH_3)_3$ with $SeCl_4$. The first product to be isolated is $(C_6H_5)_3P{-}N{-}SeCl_3$, in which another chlorine is replaced to give $[(C_6H_5)_3P{=}N]_2SeCl_2$. On addition of $SbCl_5$ at −78°C, one Cl is abstracted and $[(C_6H_5)_3P{=}N]SeCl^+][SbCl_6^-]$ is formed (*389*). A Se–N dou-

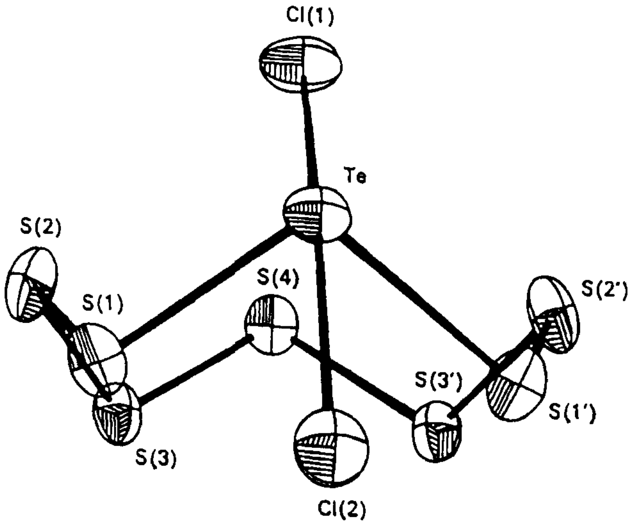
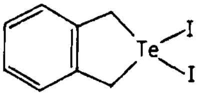


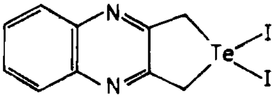
FIG. 4. Structure of the Cl_2TeS_7 molecule *(430, 431)*. Br_2TeS_7 is isostructural to it.

ble bond is to be assumed in $Cl_2Se{=}NTeF_5$, which was obtained as a reaction product from $SeCl_4$ and H_2NTeF_5 *(180)*. $[(SBr)_2N^+][AsF_6^-]$, containing the first example of a bromine-containing sulfur–nitrogen cation (with formally trivalent sulfur) was reported as a bromination product of $[S_2N^+][AsF_6^-]$ with Br_2 in SO_2 *(58)*; it is a homologue of $(SCl)_2N^+$ of which different salts have been prepared. Another interesting result in the field of chalcogen-nitrogen-halogen compounds (which are not treated here in detail) is the establishment of an exo-cyclic covalent sulfur–iodine bond in a thiazyl compound from the crystal structure of the six-membered ring compound $[(C_6H_5)_2PN]_2NSI$ *(72)*. The novel thermally unstable reagent $NSCl_3$ was generated by treatment of $(NSCl)_3$ with SO_2Cl_2, and its use as an in situ reagent (e.g., for cyanoisothiazoles) was reported *(28)*.

Recent interesting additions to the large number of investigations on organo-substituted chalcogen(IV) tetrahalides include studies on bonding and structure of $(C_6H_5)TeCl_3$ *(25, 103)*, $(C_6H_5)TeI_3$, and $(C_6H_5)_2TeI_2$ *(27)*, $(C_6H_5)_3TeCl$ *(450)*, on ^{125}Te solid-state NMR spectra, crystal structures and secondary bonding in R_3TeY compounds ($R = CH_3, C_6H_5$; $Y = Cl, I$) *(81)*, on preparation and structure of an adduct of $(CH_3)_2TeI_2$ with I_2 *(377)*, on an interesting adduct of 1,3-dihydro-2,2-diiodotellurolo-quinoxaline (**1**) with bis(bromomethyl)quinoxaline *(413)*,



(1)



(2)

and on the similar 1,1-diiodo-3,4-benzo-1-telluracyclopentane (**2**) (*239*, *287*), the latter with a comparative discussion of secondary bonding systems in organotellurium iodides. The interesting amidinato complex $PhC(NSiMe_3)_2TeCl_3$ was prepared by the reaction of *N,N,N′*-tris(trimethylsilyl)benzamidine with $TeCl_4$ (*453*).

As a final remark in this chapter, a very important investigation concerning the experimental verification of lone pair electron density has been reported for dimethyltellurium dichloride, $(CH_3)_2TeCl_2$ (*451*). High-resolution X-ray experiments on the deformation density at 151 K, which are the first ones of this kind for a heavy main-group element molecule, give clear and quantitative evidence for the localized electron density predicted at one of the equatorial positions of the ψ-trigonal bipyramidal molecule.

5. *Reactions of the Tetrahalides*

The reactions of the chalcogen(IV) halides are quite variable due to their high general reactivity, their remarkable structural and bonding properties, and the specific influence of the inert pair as an "electronic chamaeleon" on the reaction paths and products. As examples, important reaction types that will be addressed besides the ones mentioned above are (X = chalcogen, Y = halogen, R^+ = metal ions or large cations such as tetraphenylphosphonium(arsonium), triphenylmethyl, tetrabutylammonium, etc.)

XY_4 + R^+Y^- $\longrightarrow$ halo-chalcogenates(IV)
+ chalcogen(IV) oxide $\longrightarrow$ chalcogen(IV) oxide halides
+ chalcogen(IV) oxide + R^+Y^- $\longrightarrow$ oxo-halo-chalcogenates(IV)
+ reducing agents + R^+Y^- $\longrightarrow$ halo-chalcogenates(II)
+ alkyl(aryl)ating agents $\longrightarrow$ organo-chalcogen(IV) halides
+ halides BY_n as Lewis acids (bases) $\longrightarrow$ "ionic" adducts
+ aqueous conc. HY $\longrightarrow$ hydronium halochalcogenates(IV)
+ superacids $\longrightarrow$ halo-chalconium polycations

B. HALO-CHALCOGENATES(IV)

As the most straightforward reaction type, a systematic stepwise degradation of both structural classes of tetrameric X_4Y_{16} molecules

(X = Se; Y = Cl, Br and X = Te; Y = Cl, Br, I) leads to tri-, di- and mononuclear haloselenates(IV) and halotellurates(IV) (*107, 171, 172, 245, 259–261*). The products are obtained by reaction of stoichiometric amounts of the tetrahalides with halides R^+Y^- (see above) in organic solvents with low polarity. In these solvents side reactions such as oxidation or hydrolysis are avoided. In the case of Te_4Cl_{16}, as a general reaction scheme it can be proposed that at first Cl^- attacks the tetramer, eliminating one or two $TeCl_3^+$ groups from it in the form of neutral (monomeric or associated) $TeCl_4$ species according to Eq. (4) and (5):

$$Te_4Cl_{16} + R^+Cl^- \longrightarrow [R^+][Te_3Cl^-_{13}] + TeCl_4 \tag{4}$$

$$[R^+][Te_3Cl_{13}{}^+] + R^+Cl^- \longrightarrow [R^+]_2[Te_2Cl_{10}{}^{2-}] + TeCl_4 \tag{5}$$

As molecular weight determinations and conductivity data in different solvents (*38, 39, 161, 168, 220*) indicate, partial homolytic dissociation of the tetramers in solution into trimers, dimers, and monomers, the formation of $Te_3Cl_{13}{}^-$ and $Te_2Cl_{10}{}^{2-}$ can also be interpreted as an addition of one or two Cl^- to the assumed Te_3Cl_{12} and Te_2Cl_8 fragments. In Fig. 5 this series of oligomeric chlorotellurates(IV), including $TeCl_6{}^{2-}$ as the monomeric end product, is presented. Figure 6 shows an ellipsoid plot of the $Te_3Cl_{13}{}^-$ ion in the triphenylmethyl salt (*258, 260*). This type of ion with approximate C_{3v} symmetry consists of three edge-sharing distorted octahedra and has only one μ_3-halogen left in its structure besides three μ_2-halogens. Each chalcogen keeps the three strong terminal bonds so that the bonding in the ion is close to an ionic formulation $[(TeCl_3{}^+)_3(Cl^-)_4]$. [See also (*86*).] The interesting structural analogy of the $Te_3Cl_{13}{}^-$ type anions to species such as $Mo_3O_4F_9{}^{5-}$, $W_3O_4F_9{}^{5-}$, Nb_3Cl_8, $Zn_2Mo_3O_8$, or $(C_5H_5)_3Mo_3S_4$ has been discussed (*285*).

1. *Dinuclear and Trinuclear Anions*

This type of nucleophilic degradation of the tetramers with subsequent crystallization of the resulting halo-anions together with large counter-cations has been extended in recent studies to the other known tetrameric chalcogen(IV) halides, so that a rather extensive series of novel trimeric and dimeric halo-chalcogenates(IV) is known. For the selenates it includes the $Se_2Cl_{10}{}^{2-}$, $Se_2Br_{10}{}^{2-}$, and $Se_3Cl_{13}{}^-$, $Se_3Br_{13}{}^-$ ions in salts such as $[(C_6H_5)_4As]_2[Se_2Cl_{10}]$ (*261*), $[C_{14}H_{13}ClN_3]_2[Se_2Cl_{10}] \cdot 2CH_3CN$ (*378*), $[(C_2H_5)_4N]_2[Se_2Br_{10}]$ (*21*), $[(C_6H_5)_3C][Se_3Cl_{13}]$ (*21*), $[(C_6H_5)_3C][Se_3Br_{13}]$ (*21*); examples containing the $Te_2Cl_{10}{}^{2-}$, $Te_2Br_{10}{}^{2-}$, $Te_2I_{10}{}^{2-}$, $Te_3Cl_{13}{}^-$, $Te_3Br_{13}{}^-$, and $Te_3I_{13}{}^-$ ions include the salts $[(C_6H_5)_4As]_2[Te_2Cl_{10}]$ (*108*),

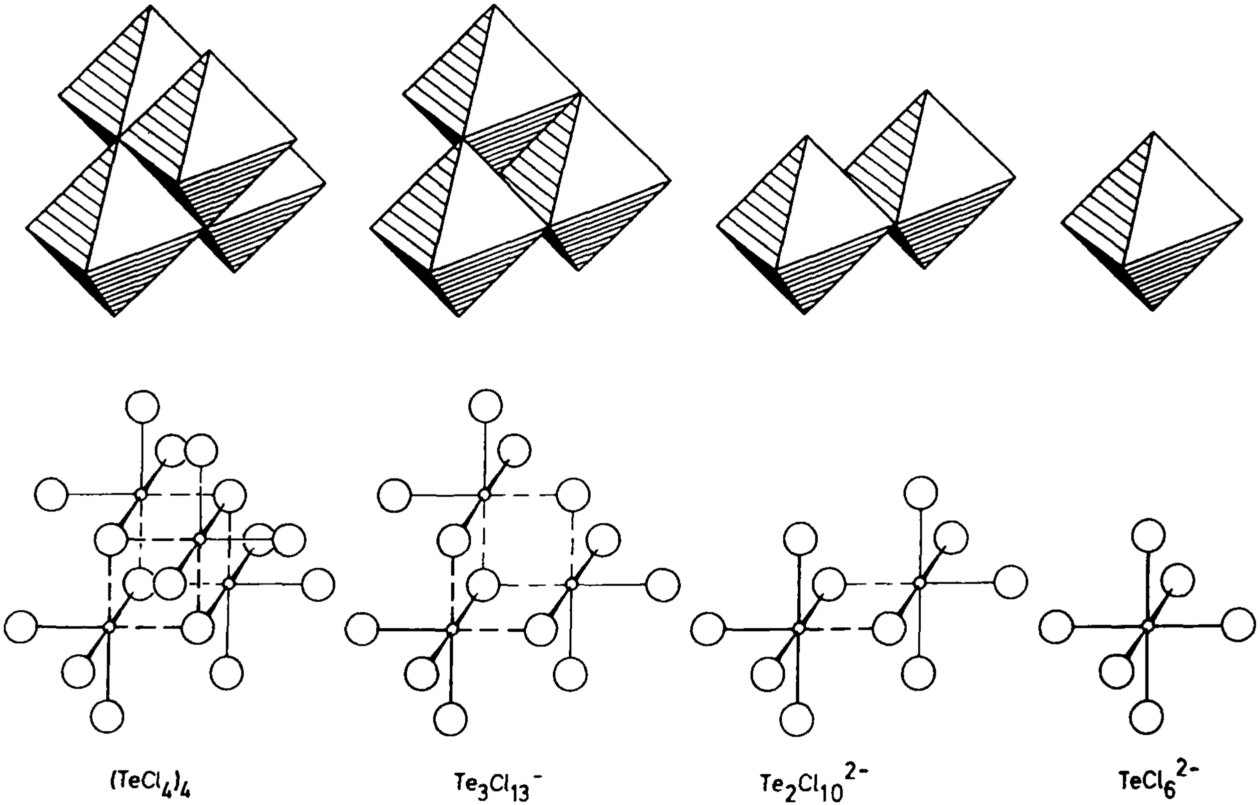


FIG. 5. Degradation of the cubane-like tetrameric chalcogen(IV) halides exemplified by the formation of $Te_3Cl_{13}^-$, $Te_2Cl_{10}^{2-}$, and $TeCl_6^{2-}$ from Te_4Cl_{16} *(244)*.

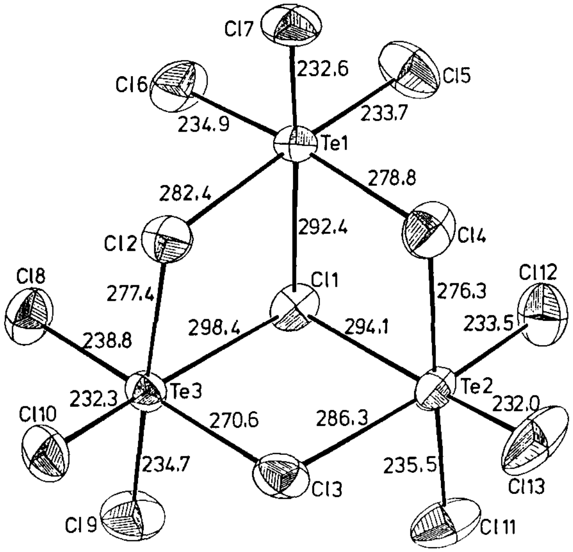
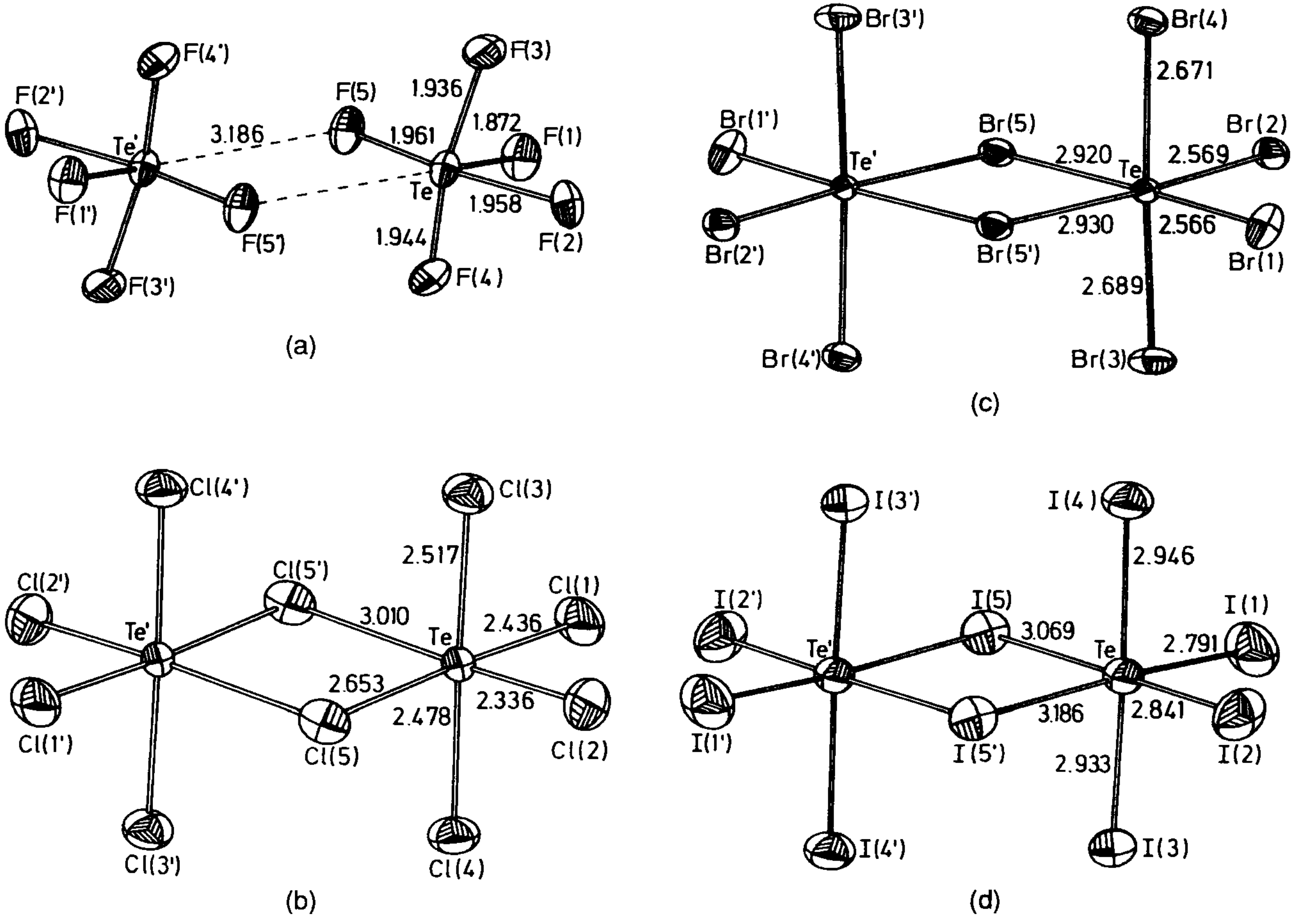


FIG. 6. $Te_3Cl_{13}^-$ ion in the crystal structure of $[(C_6H_5)_3C^+][Te_3Cl_{13}^-]$, with bond lengths (Å) (*258*).

$[(C_6H_5)_4P]_2[Te_2Br_{10}]$ (*245*), $[(C_6H_5)_4N]_2[Te_2Br_{10}]$ (*108*, *171*), $[(C_7H_7)(C_2H_5)_3N]_2[Te_2I_{10}]$ (*108*), $[(C_2H_5)_4N]_2[Te_2I_{10}]$ (*108*), $[(C_6H_5)_3C][Te_3Cl_{13}]$ (*259*, *260*; see also *86*), and $[H_9O_4][Te_3Br_{13}]$ (*108*).

Other reactions leading to dimeric and trimeric halotellurates(IV) include the interesting synthesis of $Te_2Cl_{10}^{2-}$ from triphenylphosphane-imino-tellurium trichloride $(C_6H_5)_3P{=}N{-}TeCl_3$, which is obtained from $(C_6H_5)_3P{=}N{-}Si{-}(CH_3)_3$ with $TeCl_4$, and which is reacted with $SOCl_2$ to give $[(C_6H_5)_3PCl^+]_2[Te_2Cl_{10}^{2-}]$ (*388*).

The series of the decahalotellurates(IV) that are shown in Fig. 7 (*107*, *244*, *245*, *249*) clearly demonstrate the stereochemical influence of the inert pair as a function of the halogen (*244*, *246*). The fluorine compound contains quasi-monomeric ψ-octahedral anions similar to the known alkali metal pentafluorotellurates(IV) (*43*, *166*) with almost negligible bonding interaction within the pseudo-dimer. In the series of the dimeric ions $Te_2Cl_{10}^{2-}$, $Te_2Br_{10}^{2-}$, and $Te_2I_{10}^{2-}$ the decreasing ratio of the average bridging Te–Y bond lengths as compared to the equatorial terminal ones (Cl: 1.19 Å; Br: 1.14 Å; I: 1.11 Å) indicates increasingly symmetrical bonding. As an example, for the strong stereochemical activation of the inert pair on the chalcogen by organic ligands, the


F(4')
F(2')
Te'
3.186
F(1')
F(5')
F(3')
F(5)
1.936
F(3)
1.961
1.872
F(1)
Te
1.958
F(2)
1.944
F(4)
(a)
Br(3')
Br(4)
2.671
Br(1')
Br(5)
Br(2)
2.920
Te'
Te
2.569
Br(2')
Br(5')
2.930
2.566
Br(1)
2.689
Br(4')
Br(3)
(c)
Cl(4')
Cl(3)
2.517
Cl(2')
Cl(5')
Cl(1)
3.010
2.436
Te'
Te
2.653
2.478
2.336
Cl(1')
Cl(5)
Cl(2)
Cl(3')
Cl(4)
(b)
I(3')
I(4)
2.946
I(2')
I(5)
I(1)
3.069
Te'
Te
2.791
3.186
2.841
I(1')
I(5')
I(2)
2.933
I(4')
I(3)
(d)

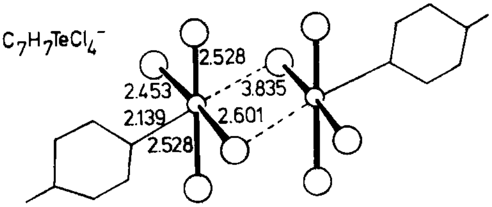


FIG. 8. Trans influence of the organo ligands in the tetrachloro-*p*-tolyltellurate(IV) anion of [4-picolinium$^+$][$C_7H_7TeCl_4^-$], with distances (Å) (*244*).

bis-*p*-tolyl-substituted derivative of $Te_2Cl_{10}^{2-}$ was shown to have an even stronger trans-bond-lengthening effect within the pseudo-dimer than in the fluorine compound (*244, 246*) (Fig. 8).

The question of the existence of discrete pentahalotellurates(IV) and pentahaloselenates(IV) (halogen is Cl, Br, or I) without any secondary bonding interaction remains open. In a recent paper monomeric tetragonal pyramidal $TeCl_5^-$ anions were proposed from the analysis of vibrational spectra of their salts with bulky cations such as tetrabutylammonium and tetraphenylphosphonium (*408*), in accordance with an earlier proposal (*345*) and with similar spectroscopic arguments for the existence of a discrete $SeCl_5^-$ anion (*268*). All crystal structures from products of these systems, however, including those with bulky cations, show more or less strong association to larger units. This is shown by the examples of $Se_2Cl_{10}^{2-}$ (*261*) (bridging Se–Cl bond lengths 2.519 and 2.803 Å) and $Te_2Cl_{10}^{2-}$ (*107, 244, 249, 388*) (Fig. 7) in the [$(C_6H_5)_4P^+$] and [$(C_6H_5)_4As^+$] salts cited above. Their Raman spectra (*107, 261*) are very similar to those given in refs. *408* and *268*, and they can be considered as being composed of two tetragonal pyramidal units associated through a halogen bridge. This association might not influence the spectra significantly if the central bridging system in the dimers is very asymmetric.

2. *Hexahalochalcogenates(IV)*

The end-products of the nucleophilic degradation reactions of the tetrameric tetrahalide molecules are the well-known octahedral species XY_6^{2-} (X = Se, Te; Y = Cl, Br, I). A large number of salts with

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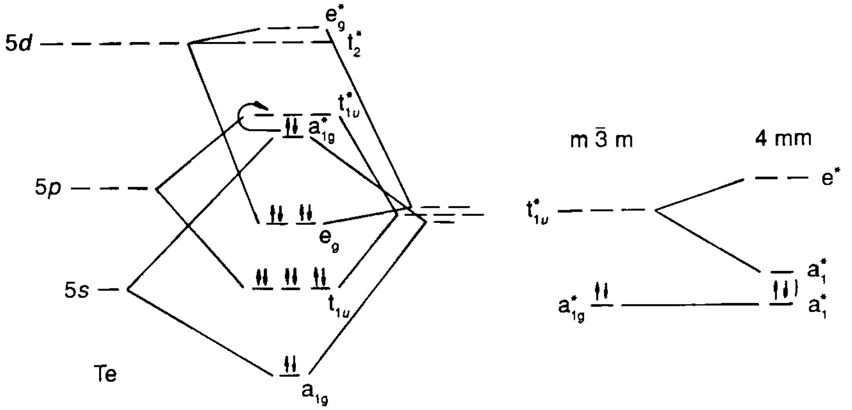
FIG. 7. Structures of (a) TeF_5^- in [$(C_2H_5)_4N^+$][TeF_5^-], (b) $Te_2Cl_{10}^{2-}$ in [$(C_6H_5)_4As^+$]$_2$[$Te_2Cl_{10}^-$], (c) $Te_2Br_{10}^{2-}$ in [$(C_2H_5)_4N^+$]$_2$[$Te_2Br_{10}^{2-}$], and (d) $Te_2I_{10}^{2-}$ in [$(C_7H_7)(C_2H_5)_3N^+$]$_2$[$Te_2I_{10}^{2-}$], with interatomic distances (Å) (*244*).

these anions has been known for some time, and they are prepared as chemically rather stable species according to different methods (*158, 159, 161, 162*). The more or less ideal octahedral symmetry of these 14-electron XY_6E systems has been a matter of controversy in past decades, and they had been quoted as exceptions from the VSEPR model (*155*). Today, their structures in different surroundings are precisely documented, and from spectroscopic and theoretical studies their bonding and structure as well as their dynamic properties are being reasonably well understood (for literature see *17, 158, 159, 161, 162, 222, 445*). Models to desribe them reach from a simple np^3nd^2 $(n + 1)s$ hybridization picture (*364*) with the inert pair shielding the bonding electrons up to a molecular orbital-based model of three orthogonal three-center four-electron bonds, both models predicting rather weak bonding (as observed). The bond lengths of the known hexahaloselenates(IV) and -tellurates(IV) are given in Table III (Section III,B).

In a number of recent papers the phenomena of dynamic and static distortion of hexahaloselenates(IV) and -tellurates(IV) have been analyzed in some detail, based on structural, spectroscopic, and theoretical investigations (*4–17*). For the $TeCl_6^{2-}$ and the $TeBr_6^{2-}$ anions it has been pointed out (*17;* see also *85*) that a dynamically distorted octahedron is stabilized for XY_6E systems such as TeY_6^{2-} if the crystal field at the Te site has at least a center of symmetry. Otherwise, a static distortion will be observed. The dynamic distortion is connected with a broadening of the IR-active T_{1u} vibrations of the octahedron (*419*), suggesting vibronic coupling between the ground state ($a_{1g}\sigma^*$) and the first excited state ($a_{1g}\sigma^*$, $t_{1u}\sigma^*$). This is shown in Fig. 9. The resulting degenerate t_{1u}^* state is stabilized by splitting and distortion of the octahedron (e.g., toward 4mm symmetry) (*45*). However, as shown by diffraction experiments on antifluorite type compounds M_2TeY_6 (M = Rb, Cs), the splitting is very small, and the averaged structure with m3m symmetry is retained even at very low temperatures (e.g., *12, 16, 17*).

Other recent investigations of octahedral hexahalochalcogenates(IV) report structural studies of phase transitions of M_2XY_6 salts with the cubic antifluorite type. They frequently undergo static symmetry reductions to tetragonal, monoclinic, and triclinic at low temperatures with different types of cooperative distortions of the arrangement of the octahedra, and they are of possible interest as ferroelastic materials, as in the case of K_2TeBr_6 (*1, 4, 5, 7, 452*). The large number of other recent papers on this class of compounds includes much structural work on salts with a variety of counter-cations (hexachloro- and hexabromoselenates: *9, 12, 276, 405;* hexahalotellurates: *30, 41, 44, 60, 62, 90,*



(a) (b)

FIG. 9. (a) Qualitative MO diagram for octahedral TeY_6^{2-}, indicating vibronic coupling of ground state and first excited state (arrow, see text); (b) Splitting of the t_{1u}^* state with tetragonal distortion of the octahedron (*17*).

92, 107, 190, 199, 225, 249, 266, 267, 292, 300, 393, 394, 424, 429; mixed-halide anions $SeCl_4Br_2^{2-}$: *172, 276*); general structural considerations (*222*); luminescence studies (*18*); and spectroscopic investigations (*13, 19, 20, 76, 86, 91, 96, 145, 167, 193, 210, 265, 345, 407*).

3. *Nonahalodichalcogenates(IV)*

If the degradation reaction of the tetramers is performed at slightly lower temperatures with very slow addition of halide as nucleophilic agent, an unexpected series of dinuclear haloselenates(IV) and -tellurates(IV), $X_2Y_9^-$ (with X = Se, Y = Cl, Br; X = Te, Y = Cl, I) was obtained; they contain three μ_2-bridging halogens, resulting in face-sharing of the two pseudo-octahedral halves of the molecule. In Fig. 10 the $Se_2Cl_9^-$ and $Te_2I_9^-$ ions in the crystal structures of $[(C_6H_5)_4As^+]$ $[Se_2Cl_9^-]$ (*261*) and $[Cu(CH_3CN)_4^+[Te_2I_9^-]$ (*107, 249*) are shown as ellipsoid plots. If the bond lengths and the geometry of the central X–Y–X bridging systems are compared to the data of transition metal halo anions of the type $X_2Y_9^{n-}$ (X = Ti, Zr, Cr, Mo, W), the possible stereochemical influence of the lone pairs at the chalcogen atoms (and missing metal–metal bonds) lead to a significant lengthening and weakening of the bridging X–Y bonds in the voluminous central XY_3X units of the halochalcogenates(IV). The $Se_2Cl_9^-$ ion was also isolated in the crystalline double salt $[(C_2H_5)_4N^+]_4[Se_2Cl_{10}^{2-}][Se_2Cl_9^-]_2$ (*261,*

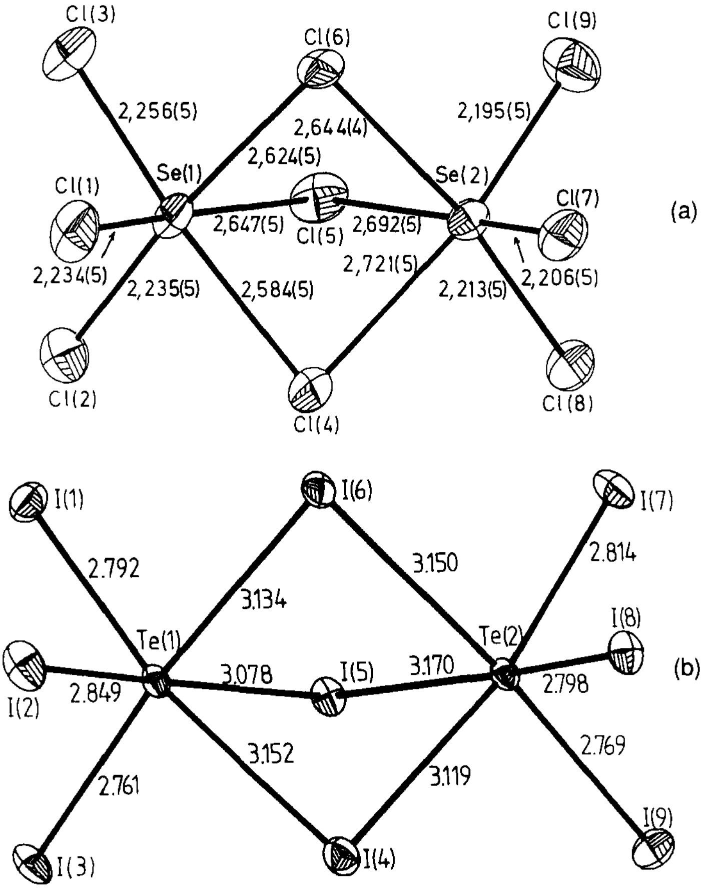


FIG. 10. (a) $Se_2Cl_9^-$ ion in the crystal structure of [$(C_6H_5)_4As^+$][$Se_2Cl_9^-$] and (b) $Te_2I_9^-$ ion in the [$Cu(CH_3CN)_4^+$][$Te_2I_9^-$] structure, with bond lengths (Å) (*108, 261*).

406). Its existence, together with evidence from Raman spectra (*261, 406*) indicates the presence of an equilibrium between $Se_2Cl_{10}^-$ and $Se_2Cl_9^-$ + Cl^- in aprotic solutions.

4. *Polymeric Species*

Two novel, remarkable polymeric halochalcogenates(IV) with intermolecular charge-transfer bonding were reported recently. The first, in a compound with the empirical composition [$(CH_3)_3NH^+$]$_2$[$SeBr_8^{2-}$] (*172, 276*), was obtained from $SeBr_4$ and trimethylammonium bromide in boiling aqueous HBr, and contains distorted $SeBr_6^{2-}$ anions that are in bonding contact to two *cis*-coordinated Br_2 molecules such that endless chains of composition $[SeBr_6^{2-} \cdot Br_2]_2$ result (Fig. 11). The bond length in the Br_2 unit is significantly elongated as compared to the free molecule, and the distortion of the $SeBr_6$ octahedron reflects the effect of intermolecular bonding (*172, 276*). The second is a polymeric iodotellurate(IV) in a compound with the empirical formula $[(CH_3)_3NH^+]_2[TeI_7^{2-}]$, which was obtained by treatment of trimethylammonium hexaiodotellurate(IV) with dilute HI at 50°C (*225*). It consists of chains of trans-corner-sharing distorted TeI_6 octahedra with bridging and terminal Te–I distances of 2.934 and 3.112 Å and has, consequently, the composition $[TeI_5^-]_n$. In addition, the crystals contain a remarkable new type of almost equidistant $[I_2^-]_n$ polyiodide chains (I–I 3.091 and 3.133 Å), so that the structural formula of the compound is $[(CH_3)_3NH^+]_2\,[TeI_5^-]_n[I_2^-]_n$.

Trifluoromethyl-substituted pentahalotellurate anions of composition $(CF_3)_2TeY_3^-$ (Y = Br, Cl) were obtained as salts $M[(CF_3)_2TeY_3^-]$ from reactions of $(CF_3)_2TeY_2$ with MY (M = K, Rb, Cs, $(CH_3)_4$, Ag) (*329*). In the series of organosubstituted pentahalo-anions, the interesting mixed square pyramidal (ψ-octahedral) $(C_6H_5)TeCl_3I^-$ anion was prepared as the $(n\text{-}C_4H_9)_4N^+$ salt by addition of iodide to phenyltellurium trichloride (*26*).

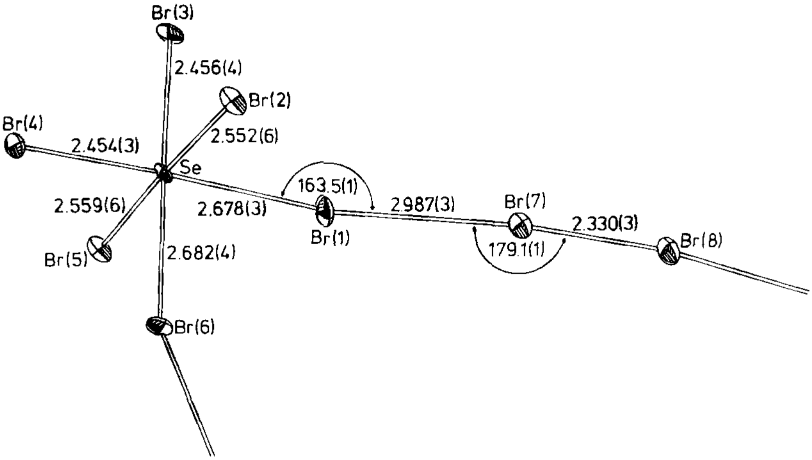


FIG. 11. Section of the polymeric $[SeBr_6^{2-} \cdot Br_2]_n$ ion in the crystal structure of $[(CH_3)_3NH^+]_2[SeBr_8^{2-}]$, with bond distances (Å) and bond angles (deg.) (*276*).

C. ADDUCTS WITH LEWIS ACIDS AND LEWIS BASES

The partial ionic character of the halides of sulfur(IV), selenium(IV), and tellurium(IV) and their ambiguous electronic behavior determines their reactivity toward Lewis acids and bases. A large number of publications in this field have appeared since the earlier work (*146, 147, 158–162, 391*) of O. Ruff and others, and the number of Lewis-base–Lewis-acid adducts of the chalcogen(IV) halides is very large. This is especially true for 1 : 1- and 1 : 2-adducts with other nonmetal and metal halides or oxide halides such as BF_3, $AlCl_3$, $GaCl_3$, $InCl_3$, $SnCl_4$, PF_5, PCl_5, $POCl_3$, AsF_5, SbF_5, $SbCl_5$, ICl_3, $TiCl_4$, $ZrCl_4$, VCl_4, $NbCl_5$, $TaCl_5$, UCl_5, $FeCl_3$, $AuCl_3$, or with oxides such as SO_3 and several others. More recent references to compounds of this class include, besides the ones discussed below, refs. (*34, 55, 56, 59, 79, 93, 97, 99, 120, 148, 149, 279, 320, 374, 375, 398*).

The resulting ternary compounds are generally obtained without difficulties from the components in aprotic solvents; alternatively, special preparation methods are employed successfully, such as the use of As_4S_4 and As_4Se_4, sulfur or S_7TeCl_2 as chalcogen sources to be chlorinated in situ during the reaction with the adduct partner (*75*). The adducts show variable and often remarkable bonding and structural properties and are of importance for different applications, for example as halogenating agents, for the stabilization of thermally labile halides, or as catalysts. A large number of recent structural investigations on this type of halide adducts show that the chalcogen(IV) halides can act, in a delicate balance with the Lewis-acidic or -basic properties of the reaction partner, as a Lewis base (halide donor) or, in much rarer cases, as a Lewis acid (halide acceptor) and that they can be characterized as being amphoteric in this sense; their electronic system and the function of the inert pairs of the chalcogens can be manipulated very sensitively by the surrounding reaction partners.

A good example of this ambivalent behavior are the adducts of $TeCl_4$ with $AlCl_3$ (*75, 247*) and PCl_5 (*79, 248*). With the Lewis acid $AlCl_3$ an adduct is formed (two modifications are known) in which $TeCl_4$ acts as a base and donates one Cl^- to $AlCl_3$, resulting in a compound with $TeCl_3^+$ and $AlCl_4^-$ units three-dimensionally connected through chlorine bridges. With PCl_5 as a reaction partner, $TeCl_4$ is the stronger Lewis acid that accepts one Cl^- and forms polymeric $(TeCl_5^-)_n$ chains built from corner-sharing $TeCl_{4+2}$ units; PCl_5 loses one Cl^- and forms isolated tetrahedral PCl_4^+ ions in the structure, in accordance with spectroscopic predictions (*38, 147*) (Fig. 12). The formation of trigonal pyramidal XY_3+ units, which are bonded more or less strongly through secondary

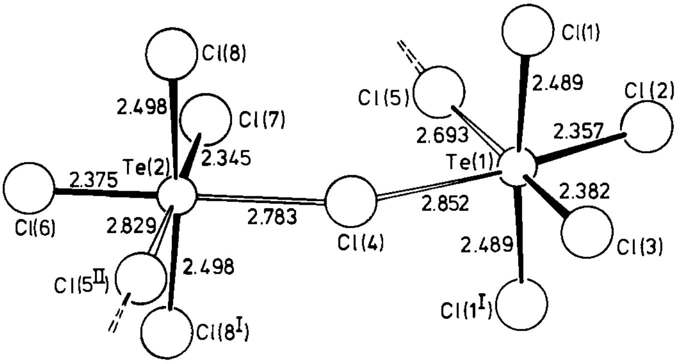


FIG. 12. Section of the $[TeCl_5^-]_n$ chains in $[PCl_4^+][TeCl_5^-]$, with bond lengths (Å) (*248*).

bonding interactions to the anionic part of the compounds, is typical for most of the adducts of sulfur(IV), selenium(IV), and tellurium(IV) halides with Lewis-acidic halides. In all cases a strongly distorted octahedral 3+3-coordination of the chalcogen is observed; the primary bond geometry of the XY_3^+ parts, including the lone pair E, can be regarded as tetrahedral XY_3E (*154*); if the secondary bonds are included, it is to be described as more or less strongly distorted octahedral $XY_3Y'_3E$.

1. *Adducts with Aluminum Trichloride, Antimony Pentachloride, and Gold Halides*

In the series of the 1 : 1-adducts of the three chalcogen(IV) chlorides with aluminum chloride, $SCl_3^+AlCl_4^-$ has been characterized (Fig. 13) (*191, 421, 382*), and a comparison is possible to the homologues $[SeCl_3^+][AlCl_4^-]$, (*418*) and to the modifications of $[TeCl_3^+][AlCl_4^-]$ (see above) (*75, 247*). According to the rules given above, the stereochemical activity of the lone pair indicated by the relative difference between primary and secondary chalcogen–halogen bonding increases strongly in the order Te, Se, S. The average values for the primary and secondary X–Y distances are 1.98 Å vs. 3.18 Å in $[SCl_3^+][AlCl_4^-]$ as compared to 2.28 Å vs. 3.06 Å in $[TeCl_3^+][AlCl_4^-]$.

The adduct $[SCl_3^+][AlCl_4^-]$ proves to be a convenient storage material for sulfur(IV) chloride, which in pure form is unstable at room temperature (see above); due to its stabilization as a trichlorosulfonium cation in the adduct, SCl_4 is thus available for preparative use at noncryogenic temperatures. The adduct is the active agent in the system $S_2Cl_2/SO_2Cl_2/AlCl_3$, which is used for chlorinations in organic syntheses; the different thermal stability of $[SCl_3^+][AlCl_4^-]$ and $[SCl_3^+]$-

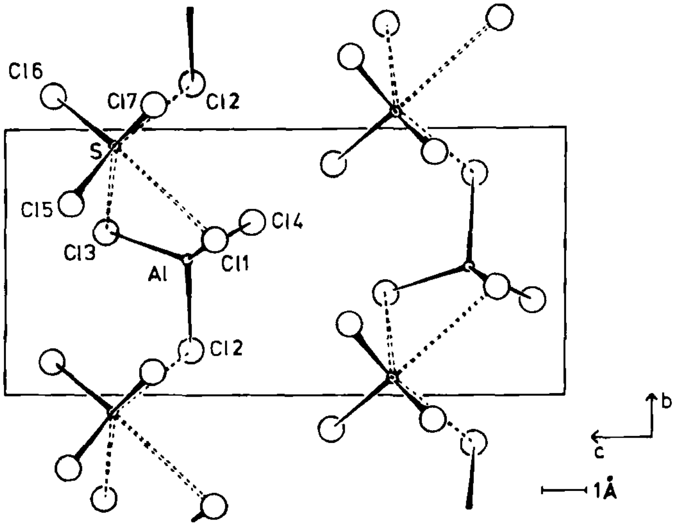


FIG. 13. Unit cell of the crystal structure of $[SCl_3^+][AlCl_4^-]$. (O) Cl, (⊙) S, and (o) Al (*244*).

$[FeCl_4^-]$ can be used for a separation of $AlCl_3$ and $FeCl_3$; anhydrous metal fluorides can be prepared using SCl_3^+ compounds (*156, 240*). Detailed ^{35}Cl nuclear quadrupole resonance studies have been reported for a number of trichlorosulfonium compounds that are in accordance with structural data on the interaction of the SCl_3^+ groups with the anions (*120, 122, 123, 179*).

Similarly, complete series of structurally characterized adducts of the chalcogen(IV) halides are, for example, the XY_4 chloride adducts with $SbCl_5$ (*75, 171, 172;* spectroscopic work: *54, 55*), adducts with gold chlorides and bromides (*119, 121, 144, 212–214*), or with iodine trichloride (*120*). They are further instructive examples for the discriminating stereochemical effects of the inert pairs of the chalcogens. $[SCl_3^+][SbCl_6^-]$, which is shown in Fig. 14, forms a structure with very little secondary bond strength. The S atoms in the SCl_3^+ groups (to be described as ψ-tetrahedral SCl_3E units) have essentially heteropolar interactions to three additional chlorines that complete the formal coordination around sulfur to a very distorted octahedron and that formally link them to the anions in a three-dimensional network (*75, 171, 172*). A completely different intermolecular arrangement with smaller differences between primary (2.10 Å) and secondary (3.13 Å) bond lengths is observed in trigonal $[SeCl_3^+][SbCl_6^-]$ (*75*). The remarkable structure of the tellurium compound is tetrameric, containing

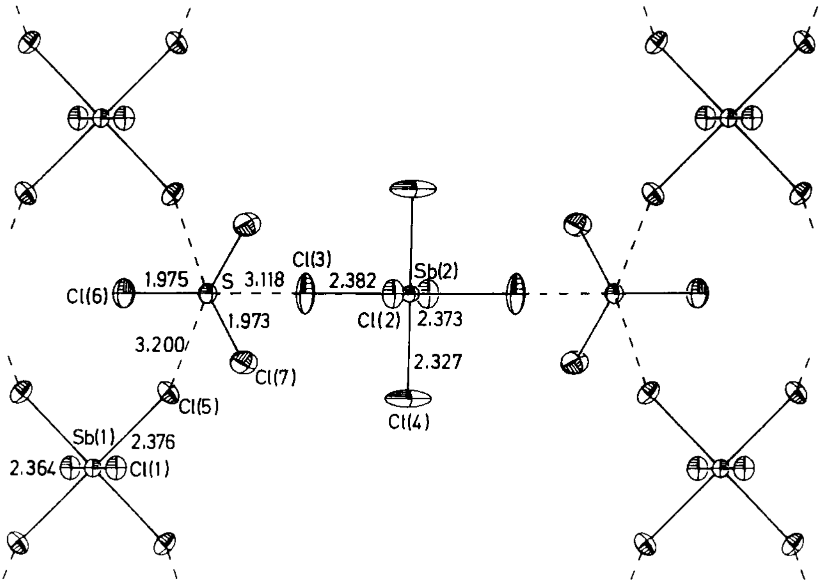


FIG. 14. Association of the polyhedra in $[SCl_3^+][SbCl_6^-]$, with distances (Å) (*172*).

$Te_4Sb_4Cl_{36}$ = $[(TeCl_3^+)_4(SbCl_6^-)_4]$ molecules with the Te and Sb atoms occupying alternating corners of a cube. The average primary and secondary Te–Cl bond lengths in the distorted $TeCl_{3+3}$ octahedra are 2.24 Å and 3.12 Å, with Sb–Cl distances of 2.38 Å in the virtually undistorted $SbCl_6$ octahedra (*171, 172;* see also *75*). A polyhedral representation of the molecule is shown in Fig. 15. As the central Te and Sb atoms in this compound are isoelectronic except for the inert pair at the tellurium, the influence of this parameter on the structure can be studied without interference of other effects.

Like the corresponding tetrachloro-iodates (*118, 120*), the adducts with gold(III) halides are examples of ternary halide systems with square planar units. In the series of the tetrachloroaurates $[SCl_3^+][AuCl_4^-]$ (*212*), $[SeCl_3^+][AuCl_4^-]$ (*214*), and $[TeCl_3^+][AuCl_4^-]$ (*213*), as well as in $[TeBr_3^+][AuBr_4^-] \cdot \frac{1}{2}Br_2$ (*144*) centrosymmetric dimers with increasing strength of secondary X–Y bonding in the order X = S, Se, Te are observed. As an example, $[(SCl_3^+)(AuCl_4^-)]_2$ is shown in Fig.16.

2. *Adducts with Arsenic and Antimony Pentafluorides*

In a number of interesting multiple-step reactions with halogen exchange, several members of the series $[XY_3^+][AsF_6^-]$ and $[XY_3^+][SbF_6^-]$ with X = S, Y = Cl, Br; X = Se, Te, Y = Cl, Br, I have

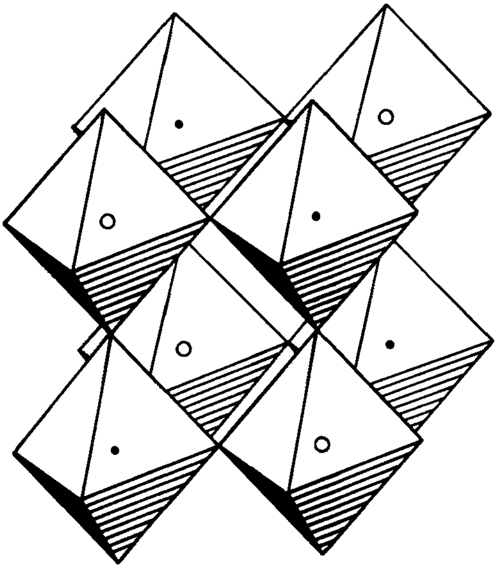


FIG. 15. Molecular structure of the adduct of $TeCl_4$ with $SbCl_5$. The $Te_4Sb_4Cl_{36}$ (i.e., $[TeCl_3^+]_4[SbCl_6^-]_4$) molecule is shown in an idealized polyhedral representation. (●) Te and (○) Sb.

been prepared; they were characterized by spectroscopic and structural methods. Successful synthetic procedures include (a) the chlorination of the chalcogens in $AsF_3/AsCl_3$ mixtures, or the reaction of SCl_2 with AsF_3 and Cl_2 (*242*); (b) the direct reaction of sulfur, chlorine, and AsF_3 under pressure (*77, 301*); (c) the bromination or iodination of sulfur,

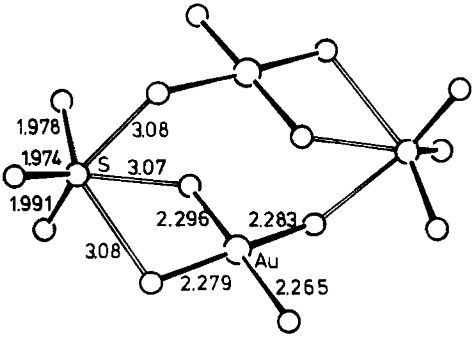


FIG. 16. Molecular structure of the tetranuclear adduct of SCl_3 with $AuCl_4$, with bond lengths (Å) (*212*).

selenium, or tellurium with Br_2 or I_2 in the presence of AsF_5 or SbF_5 in SO_2 (*50, 56, 59, 209, 321*); (d) the reaction of Se with $[I_3^+][AsF_6^-]$ (*359*); (e) the reaction of $TeCl_4$ or $TeBr_4$ with AsF_5, or the chlorination of $TeF_4 \cdot SbF_5$ with CH_2Cl_2, both in liquid SO_2 (*59, 75*); (f) the reaction of $Se_4(AsF_6)_2$, $Te_4(AsF_6)_2$, or $Se_4(SbF_6)_2$ with Br_2 in SO_2 (*59*); or (g) the reaction of $[CF_3SBr_2^+][SbF_6^-]$ with anhydrous HF (*306*). The mechanisms of all these reactions have to be explored in detail (see ref. *77*).

Crystal structures have been determined for the adducts $[SCl_3^+][AsF_6^-]$ (*301*), $[SBr_3^+][AsF_6^-]$ (*209*), $[SBr_3^+][SbF_6^-]$ (*306*), $[SeBr_3^+][SbF_6^-]$ (*349*), $[SeI_3^+][AsF_6^-]$ *209*), $[SeI_3^+][SbF_6^-]$ (*209*), $[TeCl_3^+][AsF_6^-]$ (*75*), $[TeCl_3^+][SbF_6^-]$ (*75*), $[TeBr_3^+][AsF_6^-]$ (*349*), $[TeI_3^+][AsF_6^-]$ (*356*), and $[TeI_3^+][SbF_6^-]$ (*209*). All structures contain trigonal pyramidal XY_3^+ units that are linked to the anions via three (or two, four, or five) secondary X···F bonds, resulting in more or less distorted XY_3F_3E (or XY_3F_2E, XY_3F_4E, or XY_3F_5E) coordinations of the chalcogens X (Y = Cl, Br, I; E = inert pair). According to the rules cited in Section II,A the stereochemical activity of the inert pairs at the chalcogen atoms and the differences between primary and secondary bond strengths are especially large in all these cases due to the presence of fluorine. The polarity of the interactions between XY_3^+ and the octahedral anions is higher than in the pure chloride, bromide, or iodide adducts. A detailed discussion on trends in bonding and structure of this class of compounds, including considerations on preparation methods and energetics of formation, is given in refs. (*75*) and (*209*).

$[SBr_3^+][SbF_6^-]$ is an especially interesting example for the significance of intermolecular interactions (*306*). Besides the intermolecular secondary S···F contacts, three weakly bonding Br···F contacts of 2.73, 2.86, and 2.89 Å are observed. Similar Br···F contacts are present in $[SeBr_3^+][SbF_6^-]$ (2.85, 3.01, 3.02 Å) and in $[TeBr_3^+][SbF_6^-]$ (3.05, 3.07, 3.34 Å) (*349*), and even stronger I···F interactions of 3.04 and 3.11 Å in $[TeI_3^+][AsF_6^-]$ (*356*). Among the several vibrational spectroscopic studies on the XY_3^+ moieties in the compounds $[XY_3^+][AsF_6^-]$ and $[XY_3^+][SbF_6^-]$ (*59, 75, 77, 301, 350, 397*), force constants were calculated for the XCl_3^+ ions (*397*) and a normal coordinate analysis was done for the XBr_3^+ ions (X = S, Se, Te) (*59*). The preparation and properties of SCl_3^+ compounds were discussed in a recent review (*240*).

3. *Mixed Ligand Cations*

A number of novel mixed-ligand sulfonium cations have been reported recently that are also stabilized in the solid by the weakly basic AsF_6^- as the counter-anion.

$[SF_2Cl^+][AsF_6^-]$ was prepared from the reaction of trans-CF_3SF_4Cl

and AsF_5, either as a neat mixture or in CH_2Cl_2 (*23*). In pure form it is stable for 1 week in a Kel-F tube at 25°C; in liquid SO_2 redistribution to SF_3^+ and SCl_3^+ occurs.

$[CF_3SCl_2^+][AsF_6^-]$ was obtained via oxidative chlorination of CF_3SCl with Cl_2/AsF_5 in liquid SO_2, or with ClF/AsF_5 or Cl_2F^+/AsF_5 (*310*). ClF is the chlorinating agent in all reactions, and CF_3SCl_2F is formed as an intermediate according to

$$CF_3SCl + ClF \longrightarrow CF_3SCl_2F \xrightarrow{+\ AsF_5} CF_3SCl_2^+ + AsF_6^- \qquad (6)$$

In the crystal structure at 133 K the sulfur atom has a 3+3-coordination with three secondary intermolecular S···F contacts (2.720–2.972 Å) besides the extremely long intramolecular S–C bond (1.978 Å) and two S–Cl bonds (1.959 Å). A normal-coordinate analysis supports the structural data (*310*).

Dibromomethylsulfonium salts $[CH_3SBr_2^+][A^-]$ (*313*) and dimethyl-iodosulfonium salts $[(CH_3)_2SI^+][A^-]$ (*312*) with $A^- = AsF_6^-$, $SbCl_6^-$ were synthesized via halogen exchange from the corresponding chlorosulfonium analogues with HBr or HI in liquid SO_2, or by the reactions

$$CH_3SSCH_3 + 2Br_2 + 3AsF_5 \xrightarrow{SO_2} 2[CH_3SBr_2^+][AsF_6^-] + AsF_3 \qquad (7)$$

$$(CH_3)_2S + [I_3^+][AsF_6^+] \xrightarrow{CH_2Cl_2} [(CH_3)_2SI^+][AsF_6^-] + I_2 \qquad (8)$$

Besides vibrational and NMR spectra, a crystal structure analysis is reported for $[CH_3SBr_2^+][AsF_6^-]$. Apart from a Br···F distance of 2.876 Å the trigonal pyramidal $CH_3SBr_2^+$ ion (S–Br 2.204, 2.259 Å; S–C 1.851 Å) has no significant intermolecular secondary bonding contacts (*313*).

By similar reactions of the sulfane CH_3SCF_3 with halogenating agents such as $[Cl_2F^+][AsF_6^-]$, Cl_2/AsF_5, $Cl_2/SbCl_5$, Br_2/AsF_5, or $[I_3^+][MF_6^-]$ (M = As, Sb) at low temperatures, methyl(trifluoromethyl) halosulfonium salts $[CH_3(CF_3)SY^+][A^-]$ with Y = Cl, Br, I; $A^- = AsF_6^-$, SbF_6^-, $SbCl_6^-$ have been prepared and characterized from vibrational and NMR spectra (*317*).

Analogous mixed-ligand cations of selenium have also been reported (*359*). $[(C_2F_5)_2SeI^+][Sb_2F_{11}^-]$ and the corresponding hexafluoroarsenate are prepared from bis(perfluoroethyl) diselenide and $[I_2^+][Sb_2F_{11}^-]$ or $[I_3^+][AsF_6^-]$ in liquid AsF_3; $[(C_2F_5)_2SeI^+][Sb_2F_{11}^-]$ is formed in a similar reaction using bis(perfluoroethyl) monoselenide and an excess of SbF_5 (*359*). If organoselenium and -tellurium trichlorides are reacted with $SbCl_5$, 1 : 1 adducts are formed that have the ionic structure $[RXCl_3^+]$ $[SbCl_6^-]$ (X = Se, Te; R = aliphatic and aromatic substituents) (*441*).

4. *Adducts with Oxide Halides*

Only a few chalcogen halide adducts with oxide halides are known. In the course of a systematic study on exchange reactions of transition metal oxides with SCl_2/Cl_2, paramagnetic $[SCl_3^+][MoOCl_4^-]$ was obtained and characterized (*157, 241*).

The stabilization of a novel dinuclear isomer of tellurium tetrachloride was possible by formation of an adduct with phosphorus oxide trichloride, which was prepared from solutions of $TeCl_4$ in pure $POCl_3$ (*171, 172*). The adduct molecule is shown in Fig. 17. As the Te–O distance of 2.73 Å shows, the interaction of the novel $(TeCl_4)_2$ molecule with the coordinated $POCl_3$ is only weak. From vibrational spectra and

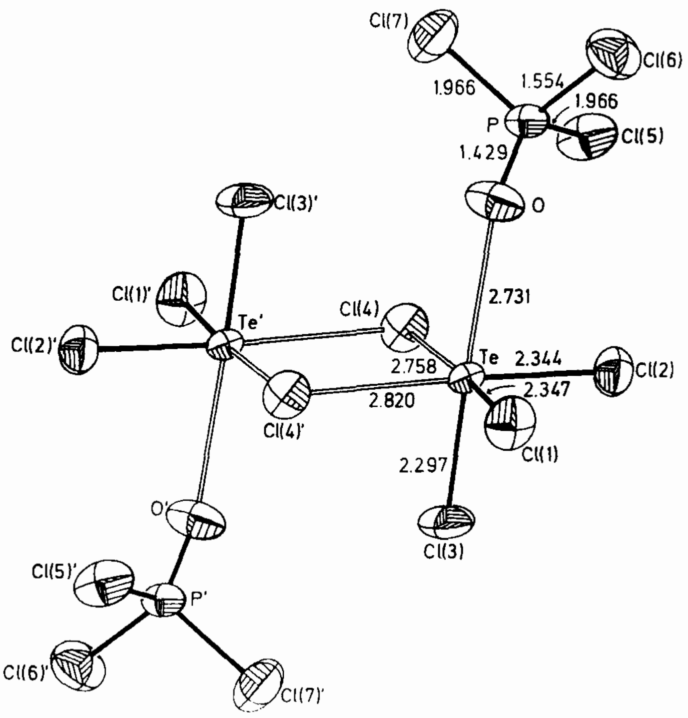


FIG. 17. Adduct of $TeCl_4$ with phosphoric oxychloride, with bond distances (Å). The dinuclear Te_2Cl_8 molecule is stabilized by weak $POCl_3$ coordination (*171*).

molecular weight determinations it follows that this reactive molecule is present also in solution (in $POCl_3$ as well as in other weakly coordinating solvents), so that it is available under these conditions for specific reactions.

D. HALO ACIDS OF THE CHALCOGENS

It has been known for some time that selenium(IV) and tellurium(IV) halides are involved in solvolytic equilibria in concentrated aqueous hydrochloric, -bromic, and -iodic acids, but there was not much insight into the nature of the products of these reactions up to some recent investigations on chloroselenate(IV) (*296*), bromoselenate(IV) (*298*), and chlorotellurate(IV) equilibria (*299*) in aqueous hydrochloric and hydrobromic acids, respectively, by UV/vis and Raman spectroscopy (see also Section II, B and E).

It is clear that the hexahalo-chalcogen(IV)-acids that result as the end-products of this solvolysis are strong Brönsted acids, in accordance with the strong tendency to form the very stable unprotonated hexahalochalcogenate(IV) anions. Besides their general interest for the chemistry of the chalcogens, the acids are important as novel candidates for the investigation of polynuclear hydronium systems in the solid state. Progress has been made in this field only recently by the isolation and characterization of at least five novel crystalline halo acids that indeed add interesting aspects to the structural chemistry of hydronium compounds.

From concentrated solutions of $SeBr_4$ in aqueous HBr a crystalline hexabromoselenous acid of composition $H_2SeBr_6 \cdot 8H_2O$ was isolated that contains regular octahedral $SeBr_6^{2-}$ dianions besides two $H_5O_2^+$ hydronium cations per dianion (*250*). The structure is shown in Fig. 18. The hydronium ions that have an intramolecular O···O distance of 2.548 Å are linked through hydrogen bridges to four additional H_2O molecules per formula unit and through OH···Br bridges (O···Br 3.42 and 3.51 Å) to neighboring anions. The structural formula of the acid has to be given as $[H_5O_2^+]_2[SeBr_6^{2-}] \cdot 4H_2O$ (*250*).

The homologous hexaiodotellurous acid of composition $H_2TeI_6 \cdot 8H_2O$ was prepared from the system $TeI_4/HI/H_2O$ in an analogous way (*218*). However, the structural arrangement in the crystal is completely different; besides regular octahedral TeI_6^{2-} dianions (Te–I 2.940 Å), interesting $H_7O_3^+$ hydronium systems with intramolecular O···O distances of 2.49 Å are observed that are again connected to the remaining H_2O molecules through somewhat weaker

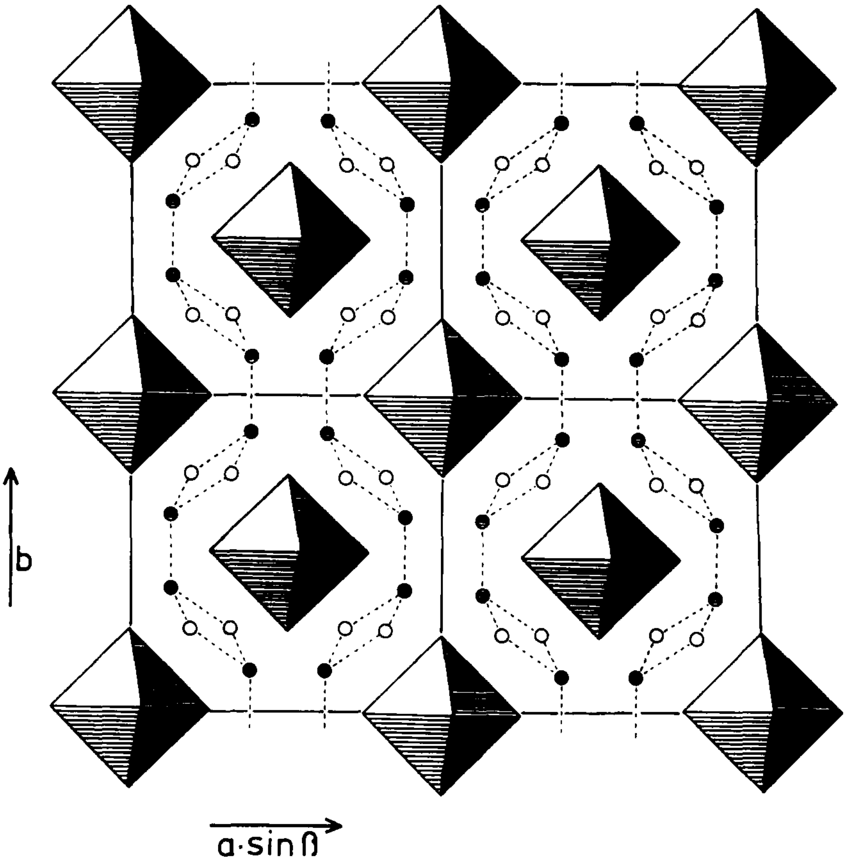


FIG. 18. Crystal structure of $[H_5O_2^+]_2[SeBr_6^{2-}] \cdot 4H_2O$ (*250*).

hydrogen bridges. The resulting structural formula is thus $[H_7O_3^+]_2$-$[TeI_6^{2-}] \cdot 2H_2O$ (*218*).

Studies to isolate novel halochalcogenous acids from nonaqueous solvents have lead to a reaction product of composition $H_2TeCl_6 \cdot 4(CH_3)_2SO$ when tellurium(IV) chloride was reacted with the system dimethylsulfoxide/HCl/H_2O (*191, 192, 427*). In the crystalline compound that was isolated from this system, protonated sulfoxide molecules (i.e., sulfoxonium cations $[(CH_3)_2SOH^+]$) are observed. They are highly interesting and had previously been postulated from strongly acidic solutions. They are present in addition to undistorted $TeCl_6^{2-}$ octahedra (Te–Cl 2.54 Å), and they are bonded to $(CH_3)_2SOH\cdots OS(CH_3)_2$ pairs with additional unprotonated Me_2SO molecules through remarkably short, however asymmetric, hydrogen bridges (O···O 2.428 Å) (see also *206*). According to its structure, the formula of the compound is $[(CH_3)_2SOH^+]_2[TeCl_6^{2-}] \cdot 2(CH_3)_2SO$.

If the $TeCl_4$: HCl concentration ratio in the system $TeCl_4/HCl/H_2O$ is kept low, a remarkable novel acid with formal composition $TeCl_4 \cdot 6H_2O$ was obtained that turned out from X-ray diffraction analysis and from vibrational spectra to have the structure $[H_9O_4^+]$ $[TeCl_4OH^-] \cdot H_2O$ (*171, 172*). The $TeCl_4(OH)^-$ hydroxo anion in this compound is the first example of a nonassociated mononuclear nonoctahedral chlorotellurate(IV) of the type XY_5E [for a related aquo-tetrachloro-hydroxo anion, see Section II,E (*80*)]. Its structure is tetragonal pyramidal (ψ-octahedral) with the OH group in the axial position (Te–O 1.929 Å, average Te–Cl 2.496 Å). It is isoelectronic and isostructural to TeF_5^-, and as fluorine in the latter anion, the OH group exerts a strong polarizing effect on the inert pair of the tellurium; the pair is stereochemically activated at the trans position to the "hard" OH ligand, in accordance with the qualitative rules cited in Section II,A. The highly interesting $H_9O_4^+$ hydronium ion in this acid is one of the few cases of a structurally precisely chacterized system of this type. In Fig. 19 the hydrogen bridge system in crystals of this compound is shown.

A recent investigation shows that halo-chalcogenous acids with higher nuclearity of the anion also can be prepared if the halide concen-

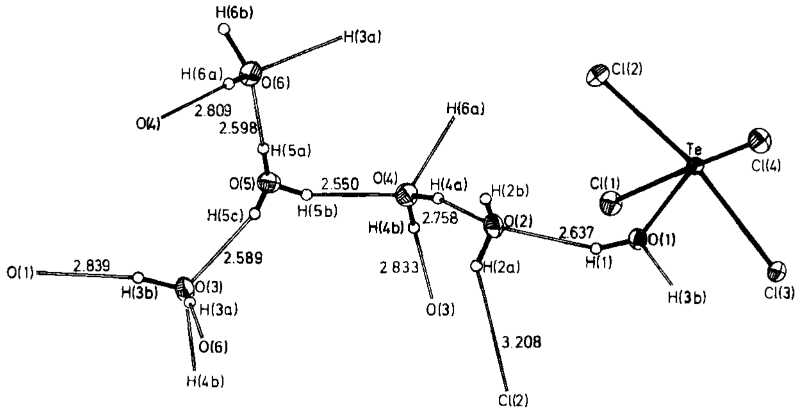


FIG. 19. Molecular structure of the anion, environment of the $H_9O_4^+$ hydronium ion, and hydrogen bridge system in crystalline $[H_9O_4^+][TeCl_4OH] \cdot H_2O$, with bond distances (Å). Oxygen atoms belonging to $H_9O_4^+$ are O(3), O(4), O(5), O(6) (*172*).

tration in the systems chalcogen(IV) halide/hydrogen halide/water is kept low enough to avoid the formation of the monomeric halogen-rich anions such as XY_6^{2-}. As the first acid with a trinuclear anion, $HTe_3Br_{13} \cdot 4H_2O$ was isolated from solutions of $TeBr_4$ in more diluted HBr/H_2O (*249*). Its structural formula is $[H_9O_4^+][Te_3Br_{13}^-]$, and it is a further valuable example of a well-characterized tetranuclear hydronium ion. The O···O distances in the $H_9O_4^+$ ion are between 2.46 and 2.58 Å. The $Te_3Br_{13}^-$ anion is of the type shown in Fig. 6, with average Te–Br bond distances of 2.512 Å in the terminal $TeBr_3$ groups, of 2.944 Å to the μ_2-bridging Br, and of 3.079 Å to the μ_3-bridging Br.

E. CHALCOGEN(IV)-HALOGEN-OXYGEN COMPOUNDS

The halo acids of selenium und tellurium are examples of the large and variable number of possible reactions of the chalcogen(IV) chlorides, bromides, and iodides with oxygen-containing compounds. Progress has been reported recently especially in the preparation and/or characterization of a number of fundamental sulfur(IV), selenium(IV), and tellurium(IV) oxygen halogen compounds. As all the species show, their extremely variable stereochemistry is largely determined by the strong polarizing effect of the hard oxygen ligands on the lone pairs of the chalcogens; this generally leads to a localization of nonbonding stereochemically active electron density in positions *trans* to the oxygen ligands. In the solid state additional intermolecular association through secondary bonding complicates the structural pattern.

1. Chalcogen Oxide Dihalides

In the low-temperature solid structures of thionyl chloride and thionyl bromide (*318*) weak intermolecular association is observed, with no significant change of the primary bonds compared to the gas phase structures determined by electron diffraction (*61, 177*) and microwave spectroscopy (*420* and refs. therein; for photoelectron spectra see *70*). The trigonal pyramidal molecules ($SOCl_2$: S–O 1.439 Å, S–Cl 2.065, 2.075 Å at 143 K; $SOBr_2$: S–O 1.42 Å, S–Br 2.203, 2.271 Å at 133 K) are linked to form two-dimensional nets in both structures, with secondary distances of 3.092, 3.176 Å (S···O), 3.490 Å (S···Cl) in $SOCl_2$, and of 3.18 Å (S···O), 3.590, 3.713 Å (S···Br) in $SOBr_2$. The gas phase ED r_a values are S–O 1.443 Å, S–Cl 2.076 Å in $SOCl_2$ (*177*) and S–O 1.448 Å, S–Br 2.254 Å in $SOBr_2$ (*61*).

Pure thionyl iodide could not be prepared yet. New UV/vis investigations on iodination products of $SOCl_2$ with HI or KI (*383*) confirmed the existence of SOI_2 in dilute solutions with an absorption maximum at

273 nm and a half-life time of 30 min at a concentration of 3.10^{-4} mol/l (*280*). Very unstable trifluoromethylsulfinyl iodide $CF_3S(O)I$ was prepared as 10^{-4} *m* solutions in *n*-hexane by iodination of $CF_3S(O)Cl$ with KI and was identified by UV/vis spectra (*303*), and the complete vibrational spectrum of the similarly reactive $CF_3S(O)Br$ was assigned (*303*).

In crystalline $SeOBr_2$ at 165 K intermolecular secondary bonding is significantly stronger than in the thionyl halides. As shown in Fig. 20 the trigonal pyramidal molecules are associated through bridging O and Br towards polymeric double chains. In the resulting quasi-octahedral 3+3-coordination of the hypervalent selenium the three additional secondary long Se···O and Se···Br distances are in the range of 2.80–3.06 Å and at 3.357 Å (*192*). The association of the molecules is in qualitative agreement with the vibrational spectra (*53*). They indicate a similar effect for $SeOCl_2$ (*62*), for which a dimeric structure was proposed in concentrated solutions (*173*).

Detailed thermodynamic studies are reported for $SeOCl_2$ (*334, 335*). The structure of the $SeOCl_2$ molecule in the gas phase has been determined by electron diffraction (*170, 448*).

2. *Oxo-Halo-Selenates*

According to recent synthetic, spectroscopic, and structural investigations, three classes of oxo-halo-selenates(IV) can be prepared with stoichiometric compositions of (a) SeO_2Y^-, (b) $SeOY_3^-$, and (c) $SeOY_4^{2-}$

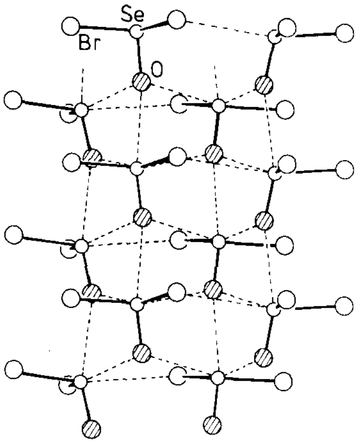


FIG. 20. Association of the trigonal pyramidal molecules in the structure of solid $SeOBr_2$ (*192, 244*).

(Y = Cl, Br) (*251, 252, 262, 268, 278, 293, 297;* for earlier work see *84, 197, 198, 346–348, 428*). The methods of preparation use (a) nucleophilic addition reactions in different stoichiometric proportions of $SeOCl_2$ or $SeOBr_2$ (or of SeO_2 for the oxygen-rich species, or of SeY_4 + small amounts of H_2O) with chloride or bromide in aprotic solvents such as CH_3CN or CH_2Cl_2; (b) solvent-free reactions, taking advantage of the autodissociation equilibria

$$2SeOY_2 \rightleftharpoons SeOY^+ + SeOY_3^- \tag{9}$$

of the oxide dihalides; or (c) direct oxidative addition reactions with haloselenates(II) (see Section II,B) such as in the case of the reaction

$$Se_2Cl_6^{2-} + O_2 \rightarrow (SeOCl_3^-)_2 \tag{10}$$

The existence of the oxygen-rich dioxo-haloselenates(IV), which are homologues of the halosulfinates in sulfur chemistry (*64*), had been predicted from spectroscopic arguments (*268*) and was confirmed by the preparation and structural characterization of crystalline $[(CH_3)_4N^+][SeO_2Cl^-]$ and $[(C_6H_5)_4P^+][SeO_2Br^-]$ (*251, 253, 406*). They are formed in a heterogeneous reaction of suspensions of SeO_2 in dry acetonitrile with dissolved halide anions; the products are subsequently crystallized with the large organo-substituted counter-cations. The anion structures of SeO_2Cl^- and SeO_2Br^- in these salts (shown in Fig. 21) (*251, 253, 406*) show remarkable differences: SeO_2Cl^- is mononuclear, trigonal pyramidal (approximate C_s symmetry as to be expected for an $XY_2Y'E$ system with one stereochemically active lone pair E), with strong Se–O bonds and a relatively weak Se–Cl bond; the closely related SeO_2Br^-, however, is associated through bridging bromine to polymeric chains, the coordination of the selenium remaining

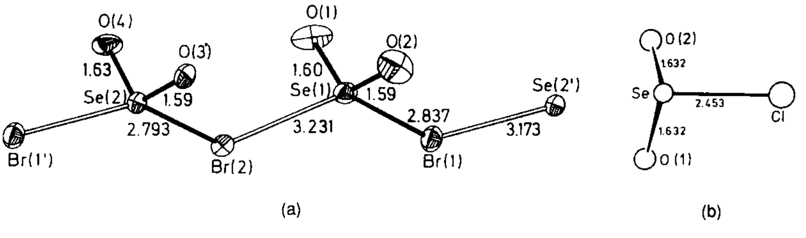


FIG. 21. The two isomeric $(SeO_2Br^-)_n$ and SeO_2Cl^- ions in the crystal structures of (a) $[(C_6H_5)_4P][SeO_2Br]$ (b) $[(CH_3)_4N][SeO_2Cl]$, with interatomic distances (Å) (*251*).

strongly asymmetric. It is to be assumed that this difference in structures is a result of crystal packing rather than of intrinsic electronic necessity; and it is another example of the stereochemical flexibility and wide variability of the chalcogen inert-pair systems as a function of the electronic environment, apparently without much change in total energy.

The electron density distribution in the SeO_2Cl^- anion of $[(CH_3)_4N^+][SeO_2Cl^-]$ has been studied by an X–X deformation density analysis using high-angle diffraction data at 120 K (*405, 406*). The deformation density maps clearly reveal the presence of lone-pair (E) density (maximum of $0.40 \pm 0.04\ e^- \times Å^{-3}$ at a distance of ca. 0.75 Å from Se) consistent with model predictions for an approximately ψ-tetrahedral SeO_2ClE arrangement with additional π density in the Se–O bonds and with a rather polar Se–Cl bond.

The variability of the inert pair systems is also evident in the class of the more halogen-rich oxo-trihaloselenates(IV), as shown from a number of recent structural and spectroscopic studies (*251, 252, 262, 268, 297*). They were prepared essentially according to the methods (a) and (c) indicated above. Depending on the counter-cation, the three different isomers of the $SeOY_3^-$ ion shown in Fig. 22 could be isolated and structurally characterized. In $[C_9H_8NO^+][SeOCl_3^-]$ with 8-hydroxochinolinium as the cation (*84*), polymeric chains are observed with distorted square $SeOCl_4$ pyramids that have an apical Se=O bond (1.59 Å), two *cis* chlorines at 2.25 Å and two bridging Cl at 2.96 and

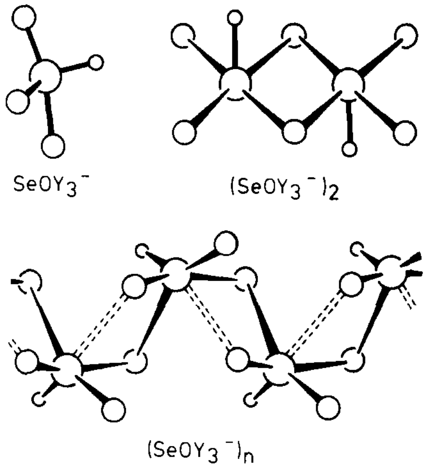


FIG. 22. The three isomeric forms of oxo-trichloroselenates(IV) (*244*).

2.99 Å from the Se. In $[(C_6H_5)_4As^+][SeOCl_3^-]$ the anion is mononuclear with a simple tbp structure, the oxygen and the lone pair being located in equatorial positions (*192, 252*). The third $SeOY_3^-$ isomer is dinuclear; it is present as $(SeOCl_3^-)_2$ in the crystals of $[(C_2H_5)_4N^+][SeOCl_3^-]$ and of $[(C_6H_5)_4P^+][SeOCl_3^-]$, and as $(SeOBr_3^-)_2$ in crystalline $[(C_6H_5)_4P^+][SeOBr_3^-]$ and $[(C_6H_5)_4As^+]$-$[SeOBr_3^-]$ (*251, 252, 262*). The centrosymmetric dianions consist of two edge-sharing tetragonal pyramidal $SeOY_4$ groups (ψ-octahedra) with the inert pairs at Se in *trans* positions to the strongly bonded axial oxygen ligands. The halogen bridge bonding in the central Se is more or less asymmetric. The structure and bond lengths of $(SeOCl_3^-)_2$ are shown in Fig. 23.

The addition of a second halide to $SeOCl_2$ according to the formal reaction

$$SeOCl_2 \xrightarrow{+\,Cl^-} SeOCl_3^- \xrightarrow{+\,Cl^-} SeOCl_4^{2-} \qquad (11)$$

leads to oxo-tetrachloroselenates(IV) with tetragonal pyramidal $SeOCl_4^{2-}$ anions with oxygen in the axial position. In the dipyridinium salt $[C_{10}H_8N_2H_2^{2+}][SeOCl_4^{2-}]$ (Se=O 1.63 Å; Se–Cl 2.25, 2.48, 2.48, 2.99 Å) the anions are distorted by participation of one of the Cl ligand atoms in strong Se–Cl···H–N hydrogen bridges to the cations (*428*). Regular pyramidal $SeOCl_4^{2-}$anions with Se=O 1.602 and Se–Cl 2.482 Å are observed in the pyridinium double salt $[(C_5H_6N^+)_4(H_3O^+)(SeOCl_4^-)_2Cl^-] \cdot 11H_2O$ (*191, 192*).

A polynuclear anion of a different kind was prepared in connection with earlier systematic investigations on adducts of $SeOCl_2$ with other halides (see, e.g., *197*) from 1:5 mixtures of $[(CH_3)_4N]Cl$ and $SeOCl_2$ (*198*). It contains two Cl^- ions which are solvated by 10 $SeOCl_2$ mole-

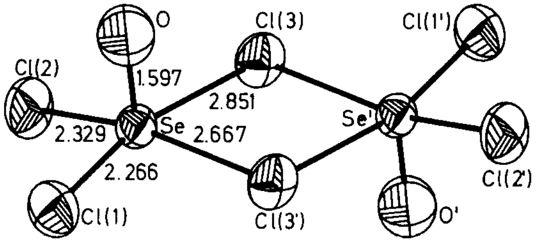


FIG. 23. Molecular structure of the $(SeOCl_3^-)_2$ ion in $[(C_6H_5)_4P^+][SeOCl_3^-]$, with bond lengths (Å) (*244*).

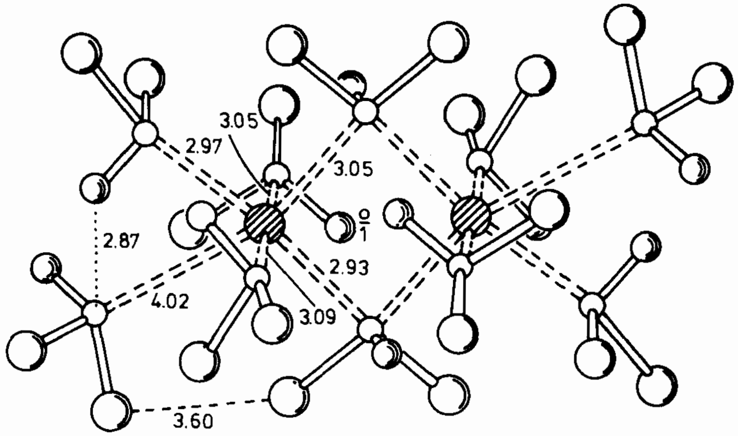


FIG. 24. Arrangement of the $SeOCl_2$ molecules around the solvated chlorides in the polynuclear anion of $[(CH_3)_4N^+]_2[(Cl^-)_2(SeOCl_2)_{10}]$. The Se···Cl distances are given (Å)(*198*).

cules in a way that each Cl^- is octahedrally surrounded bis six $SeOCl_2$, two of which are shared by an adjacent octahedron. The remarkable structure is shown in Fig. 24.

3. *Equilibria in Aqueous Solutions*

The equilibria in aqueous HCl/SeO_2 and HBr/SeO_2 solutions show that the Se(IV) species in 4-12 M HCl is $SeOCl_2$ and not a chloroselenate(IV) ion. At higher HCl concentrations probably $SeCl_5^-$ is existent in solution before $SeCl_6^{2-}$ is formed as the end product (*296*). The aqueous HBr/SeO_2 solutions have been shown to contain H_2SeO_3, $HSeO_2Br$, $SeOBr_3^-$, $SeBr_5^-$, and $SeBr_6^{2-}$ (*294*); and in the aqueous TeO_2/HCl system, $TeCl_6^{2-}$, $Te(OH)Cl_4^-$, and a monochlorotellurate(IV) of probable composition $TeCl(OH)_4^-$ are proposed to be present (*299*).

4. *Tellurium–Oxygen–Halogen Compounds*

The chemistry of the oxide chlorides, bromides, and iodides of tetravalent tellurium is in marked contrast to the more variable chemistry of corresponding more acidic sulfur and selenium compounds. One of the reasons seems to be the reluctance of Te(IV) to form stable Te═O double bonds in condensed systems. In contrast to the numerous oxohaloselenates(IV) with strong Se═O bonding, or to compounds such as $SOCl_2$, SO_2Cl_2, SO_3Cl^- and their homologues, no comparable Te analogues with mixed O/Cl, O/Br, or O/I coordination in the condensed phase could be prepared yet. $TeCl_4(OH)^-$ (Fig. 19), as the only known member of this class in solid compounds, is protonated and has a Te–O single bond. Apart from the acid $[H_9O_4^+][TeCl_4(OH)^-]$ (*172*) (see Section II,D) it has been observed, in a slightly modified form, in $[(C_6H_5)_4As^+][TeCl_4(OH)(H_2O)^-]$. Because of crystallographic disorder and of the incompletely characterized hydrogen-bond system, an alternative formulation $[TeCl_4O^{2-}(H_3O^+)]$ cannot be excluded (*80*).

As high-melting-point solid state coordination polymers the oxygen-rich phases $Te_6O_{11}Cl_2$ and $Te_6O_{11}Br_2$ were obtained in the systems $TeO_2/TeCl_4(TeBr_4)$ (*223, 336, 338, 342, 395*). Like TeO_2 they could be prepared in crystalline form by chemical transport with $TeCl_4$ (see Section II,A). Their crystal structures are largely determined by the polymeric Te–O system without any signs of Te═O double bonding; similar to the $Te_6O_{11}Br_2$ structure (*224*), the $Te_6O_{11}Cl_2$ structure (*2, 3*) contains infinite $[(Te_{12}O_{22})^{4+}]_n$ chains with essentially ionic interactions to the Cl^-; besides ψ-trigonal bipyramidal TeO_4 polyhedra, one Te in the asymmetric unit has a ψ-octahedral TeO_3Cl_2 coordination with Te–Cl distances of 3.00 Å.

In the present context it is especially interesting that there is conclusive evidence for the existence of monomeric $TeOCl_2$ and $TeOBr_2$ as primary transporting agents in the gas phase at elevated temperatures. Besides the above oxide halides, especially TeO_2 is transported in this way. These investigations permitted characterization of $TeOCl_2(g)$ (*333, 338, 343, 402*), $TeOBr_2(g)$ (*342*), as well as $TeOI_2(g)$ (*339*) by equilibrium measurements and thermodynamic data. This method of chemical transport using the $TeCl_4/TeCl_2 + Cl_2/TeOCl_2$ system has been developed for the preparation of a variety of pure crystalline metal oxides (*402, 403* and lit. cited therein; *150, 151*).

5. *Alkoxylate Complexes*

A further class of novel anionic selenium(IV)- and tellurium(IV)-halogen compounds with additional oxygen coordination was reported with organic alcoholate ligands. They are prepared by reactions of the tetrahalides with an excess of anhydrous alcohols at low temperatures and subsequent addition of halides of large cations. Examples are (a) the tetragonal pyramidal $SeCl_4OR^-$ and $TeCl_4OR^-$ ions ($R = CH_3$, C_2H_5, C_5H_9) with the Se–O and Te–O single bond *trans* to the inert pair, and (b) the $[TeCl_3(OC_2H_4O)^-]$ ion with the bidentate chelating deprotonated glycolate ligand occupying the apical and one of the equatorial positions of a similar tetragonal pyramidal coordination (*68, 406*). In Fig. 25 the structures of two of the anions are shown. For earlier work on neutral $XY_n(OR)_{4-n}$ compounds see (*288, 289, 385*).

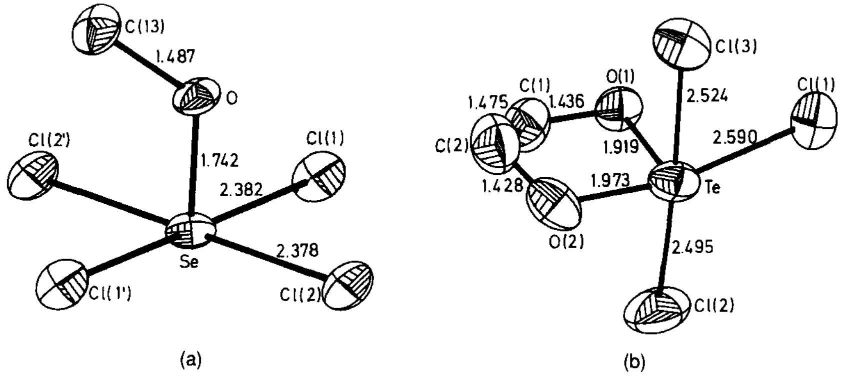


FIG. 25. Molecular structures of anionic halo-alkoxo-chalcogenates(IV), with bond distances (Å); (a) the tetrachloromethoxoselenate(IV) ion in $[(C_6H_5)_4P^+][SeCl_4OCH_3^-]$; (b) the trichloro(dioxo-ethylene-O,O′)tellurate(IV) ion in $[(C_6H_5)_4P^+][TeCl_3(OC_2H_4O)^-]$ (*68*).

III. Chalcogen(II) Compounds

A. BINARY HALIDES

As compared to the chemistry of the selenium(IV) and tellurium(IV) halides, knowledge of the reactions and stability of the corresponding halides with divalent chalcogens (oxidation number +2 for the normal dihalides, or +1 for the halides Y–X–X–Y) is less well developed.

In contrast to the well-known halosulfanes SCl_2 and SBr_2 it has not been possible yet to prepare the chlorides, bromides, and iodides of Se(II) and Te(II) as pure liquids or as pure phases in the solid state (*32, 158, 160, 161, 192;* for a critical account on the tellurium compounds see *237*). However, they exist as dissociation products of gaseous, liquid, or solid chalcogen(IV) halides in the vapor phase as well as in organic solvents (*158, 160, 180, 203, 275, 278, 298, 344, 447*) or in systems such as (selenium + SeO_2) in aqueous HCl (*278*), or in aqueous HBr (*454*). Under some of these conditions, the corresponding halogen is present according to the equilibria

$$XY_4\,(\text{g or s}) \rightleftharpoons XY_2(\text{g}) + Y_2(\text{g}) \qquad \begin{array}{l} X = \text{Se};\ Y = \text{Cl, Br}; \\ X = \text{Te};\ Y = \text{Cl, Br, I} \end{array} \qquad (12)$$

(*334, 338–341*). Their existence is shown, for example, by vapor pressure measurements in the respective systems (*340, 341*), by investigation on the chemical transport experiments (*63, 341, 403*), or by He(I) photoelectron and vibrational spectroscopic studies (*94, 326, 327, 344*). The assignments of the PE spectra are consistent with the results of theoretical VEOMP calculations (*326, 327*). The molecular structures of $SeCl_2$, $SeBr_2$, $TeCl_2$, and $TeBr_2$ were determined by electron diffraction (*22, 113, 114, 390*). Additional earlier literature is given in ref. *158, 161, 162*. The bond distances, as reference values for two-electron two-center chalcogen(II)–halogen single-bond lengths, are given in Table II together with the bond angles in the molecules.

1. *Sulfur Dihalides*

In the field of sulfur dihalides it has been shown that the short-lived SBr_2 molecule can be generated from the elements in the ionization chamber of a PE spectrometer, where it is present along with S_2Br_2 and Br_2 (*95, 325*). According to matrix-IR and mass spectrometric investigations, it is also formed via microwave discharges in SCl_2/Br_2 mixtures (*116, 202*). It has been pointed out (*305*) that thermolysis of $[SBr_3^+][AsF_6^-]$ (in a way analogous to $[SCl_3^+][AsF_6^-]$) (*78*) to SBr_2, BrF,

TABLE II

STRUCTURAL DATA OF CHALCOGEN HALIDES OF THE TYPES XY_2 AND X_2Y_2

Compound	Method[a]	X–X distance (Å)	X–Y distance (Å)	Bond angle (°)	Dihedral angle (°)	Reference
SCl_2(g)	MW		2.0140(7)	102.74(3)		*432*
SCl_2(s)	XD		2.014(av.)	102.41(av.)		*233*
$SeCl_2$	ED		2.157(3)	99.6(5)		*113*
	ED		2.18(2)			*22*
$SeBr_2$	ED		2.32(2)			*22*
	PE		2.40	100		*325*
$TeCl_2$	ED		2.329(3)	97.0(6)		*114*
$TeBr_2$	ED		2.51(2)	98(3)		*390*
S_2Cl_2	XD	1.9425(7)	2.0667(7)	107.11(3)	84.82(5)	*232*
			2.0762(9)	106.64(3)		
S_2Cl_2	MW	1.950(1)	2.0552(7)	107.66(5)	85.24(10)	*282*
S_2Br_2	XD	1.948(2)	2.237(1)	109.16(7)	83.9(1)	*232*
Se_2Cl_2	XD	2.2324(6)	2.202(1)	104.00(3)	87.41(5)	*232*
α-Se_2Br_2	XD	2.258(2)	2.357(2)	107.23(8)	85.0(1)	*232*
β-Se_2Br_2	XD	2.241(1)	2.366(1)	103.86(5)	86.41(8)	*232*
			2.369(1)	104.51(5)		

[a] XD, X-ray diffraction; MW, microwave; PE, photoelectron; ED, electron diffraction.

and AsF_5 is a convenient source of SBr_2 for gas-phase investigations of this very reactive species. Using this method, thermodynamic data (enthalpies of formation, bond energies, ionization potentials) for SBr_2 (*305*) and for SCl_2, S_2Cl_2, and S_2Br_2 (*211, 221, 283*) were determined from photoionization mass spectra. Harmonic force field calculations are reported for SCl_2 (*47*). From a comprehensive Raman spectroscopic study of sulfur chlorides in the temperature range −140 to +25°C, the temperature dependence of the concentrations of SCl_2, S_2Cl_2, SCl_4, and Cl_2 was determined, and the intense Raman effect of SCl_4 is recommended to detect small amounts of Cl_2 in SCl_2 (*416;* see also *396*).

The new compound SFCl was prepared by UV photolysis of FC(O)SCl in argon matrix and by UV photolysis of Cl_2/SF_3SF in the gas phase and characterized by detailed vibrational analysis in the matrix (*436*).

In the course of a recent low-temperature study of the system S/Cl it was possible to prepare single crystals of SCl_2 and to determine the solid-state structure at −134°C (*233*). As shown in Fig. 26, there are two independent angular molecules in the unit cell that are weakly associated through S···Cl and S···S contacts to form bimolecular layers and that have intramolecular dimensions very close to the values of the free gaseous molecule (*322, 432*) (Table II). Additional literature on properties of the chalcogen dihalides is abstracted in (*160*).

Some clarifying preparative and spectroscopic work has been reported on the existence and properties of iodosulfanes. Earlier UV/vis-spectroscopic studies have proposed diiododisulfane and diiodopolysulfanes S_nI_2 ($n = 2 \ldots 6$) to exist as more or less short-lived species in solution (*111*). Solid disulfur diiodide in a mixture with other products

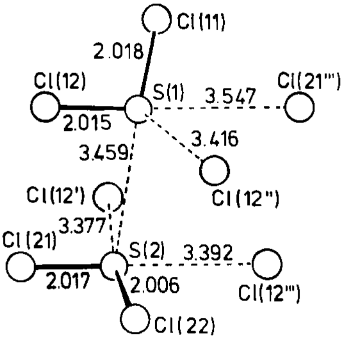


FIG. 26. Weak association of the SCl_2 molecules in the solid state structure of sulfur dichloride, with interatomic distances (Å) (*233*).

was now shown to be present in the product obtained from the reaction of HI with S_2Cl_2 at −90°C; in the IR spectrum at −105°C, bands at 510, 305, and 295 cm^{-1} are assigned to S_2I_2 (*264, 423*). New measurements of UV/vis spectra confirm the formation of S_2I_2 via exchange reactions of S_2Cl_2 or S_2Br_2 with NaI, KI, or HI in pentane or in CS_2 at low temperatures and at room temperature with a lifetime of minutes to hours (*280, 286, 423*). Excess of HI leads to decomposition according to

$$S_2I_2 + 4HI \rightarrow 2H_2S + 3I_2 \qquad (13)$$

Diiodomonosulfane SI_2 could not be obtained under similar conditions by exchange reactions using SCl_2. It disproportionates immediately according to

$$2SI_2 \rightarrow S_2I_2 + I_2 \qquad (14)$$

Similar results were obtained for the very short-lived SBr_2 (*280*).

The products of thermal decomposition of diiododisulfane are determined by its tendency to eliminate I_2 with formation of a S–S bond (*286, 304*). In concentrated solutions S_2I_2 decomposes with formation of S_6, S_8, and higher sulfur isomers according to the scheme (*286*)

$$S_2I_2 + S_2I_2 \longrightarrow S_4I_2 + I_2 \qquad (15)$$

$$S_2I_2 + S_4I_2 \longrightarrow S_6I_2 + I_2 \qquad (16)$$

$$S_6I_2 \longrightarrow S_6 + I_2 \quad \text{etc.} \qquad (17)$$

This method, by reaction of S_2Cl_2 with KI in CS_2 and subsequent in situ thermal decomposition of the resulting S_2I_2, is well suited for the preparation of large quantities of S_6 and of higher even-membered sulfur rings such as S_{12}, S_{18}, or S_{20} (*286*). In dilute solutions reactions (15)–(17) dominate, and S_6 is the principal product (*304*). Odd-membered sulfur rings such as S_7 and S_9 are formed only if SCl_2 is used as the starting substance (*286*). This proves the intermediate presence of short-lived SI_2, which decomposes according to Eq. (14) and further to

$$S_2I_2 + SI_2 \longrightarrow S_3I_2 + I_2 \qquad (18)$$

$$2\,S_2I_2 \longrightarrow S_4I_2 + I_2 \qquad (19)$$

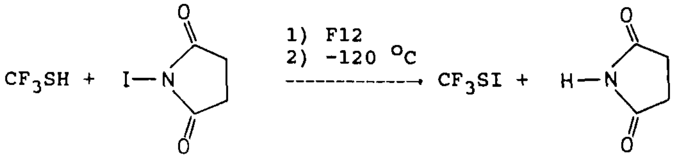
$$S_4I_2 + S_3I_2 \longrightarrow S_7I_2 + I_2 \qquad (20)$$

$$S_7I_2 \longrightarrow S_7 + I_2 \quad \text{etc.} \qquad (21)$$

The detailed analysis of the kinetics of the strongly temperature-dependent decomposition of S_2I_2 observes a first order reaction for the initial rate-limiting step and confirms the proposed subsequent competing secondary elimination-condensation reactions (*304*).

2. *Substituted Chalcogen Dihalides*

As the first fully characterized iodosulfane, pure orange-yellow trifluoromethyliodosulfane CF_3SI was prepared from *N*-iodo-succinimide and trifluoromethanethiol (*302*):



(22)

Other low-temperature exchange reactions, for example, of CF_3SCl with HI or NaI, or $Hg(SCF_3)_2$ and CF_3SH with ICl, result only in impure products. Solid CF_3SI is stable below −90°C; dilute solutions are stable for some hours at room temperature. It decomposes thermally to disulfane and I_2, and its chemical properties resemble those of ICl (*302*), in accordance with the chemical similarity of the CF_3S group with Cl (*175*). An investigation of the decomposition kinetics of CF_3SI indicates a strongly temperature-dependent second-order reaction in the rate-limiting step (*304*).

The gas-phase molecular structures of CF_3SF, CF_3SCl (*332*), and of CF_3SBr (*307*) were determined from electron diffraction experiments. Vibrational spectra and harmonic force field calculations were reported for CF_3SCl (*47*). For CF_3SBr an improved method of preparation from CF_3SCl and HBr was developed, and a full normal coordinate analysis was performed and thermodynamic functions were derived on the basis of a modified assignment of the vibrational spectrum (*42, 307*).

In contrast to the corresponding chloro compounds our knowledge of organo-substituted iodosulfanes is rather restricted. This class of compounds has received increasing attention in recent years because of their biochemical interest. Monoiodosulfanes are proposed as intermediates in the iodination of tyrosine (*206, 207*), and relatively stable iodosulfanes are reported in tobacco mosaic virus and in other proteins (*87, 88, 141*). The relatively stable triphenylmethyliodosulfane $(C_6H_5)_3CSI$ (*174*) could be crystallized at 198 K, and the first structure determination of a sulfane with a S–I bond was possible (*314*).

The intramolecular S-I bond length is 2.406 Å, which is slightly longer than in the iodosulfonium salts $[S_7I^+][SbF_6^-]$ (2.342 Å) (*352*), $[(S_7I)_2I^{3+}][SbF_6^-]_3 \cdot 2AsF_3$ (2.314 Å) (*354*), and $[S_7I^+]_4[S_4^{2+}][AsF_6^-]_6$ (2.314 Å) (*354*). In addition, there is a strong intermolecular S···I bonding contact of 3.210 Å, completing a trigonal pyramidal coordination around sulfur (*314*). In the crystal structure of the homologous bromosulfane $(C_6H_5)_3CSBr$, which was also reported recently (*309*), no such intermolecular contacts are observed, the S–Br bond length of 2.169 Å indicating slightly higher bond order than in the iodine compound. The vibrational spectra of the triphenylmethyl-halosulfanes $(C_6H_5)_3CSY$ (Y = Cl, Br, I) are also reported and assigned in that paper. The S–Y vibrations are located at 521 (Cl), 420 (Br), and 370 (I) cm^{-1} (*309*).

Iodo(trifluoroacetyl)sulfane $CF_3C(O)SI$ was reported to be stable below −78°C, and it was prepared from iodination of $CF_3C(O)SH$ with *N*-iodo-succinic imide (*316*). Its identification was based on comparison of its Raman spectrum with those of $CF_3C(O)SCl$ and $CF_3C(O)SBr$.

A stabilization of the chalcogen(II) dihalides is possible by complexation with various electron pair donors (see Section III,D). A stabilization of the simple molecular species is also obtained if the halogens are substituted by pseudo-halogens. This situation is similar to the anionic halo- and pseudo-haloselenates(II) (Section III,B). As examples, $Se(CN)_2$, $Se(SCN)_2$, and $Se(SeCN)_2$ could be prepared in crystalline form (*182, 273*). In $Se(SCN)_2$ and $Se(SeCN)_2$ the molecules are linked via secondary Se···N bonds to form chains, with a distorted square planar coordination of 2 S(Se) and 2 N around the central Se (*182*).

A number of studies of interest on other functional derivatives of the chalcogen dihalides include the preparation of novel haloselenium and halotellurium trithiocarbonates, RSC(S)SSeBr, RSC(S)STeBr, and RSC(S)STeI, as bromination and iodination products of selenium and tellurium bis(trithiocarbonates) $[RSC(S)S]_2X$ (X = Se, Te) (*216*), the synthesis of corresponding dithiocarboxylates RC(S)SSeY (Y = Br, I) and RC(S)STeY (Y = Cl, Br, I) by similar reactions with selenium and tellurium dithiocarboxylates as starting materials (*215*), the preparation of the C-brominated sulfenyl bromide, $(CF_3)_2C(Br)SBr$, by the reaction of $(CF_3)_2C{=}SO$ with hydrogen bromide (*409*), and an electron diffraction study of ClSC(O)Cl (*411*).

3. *Dichalcogen Dihalides*

Precise structural data have been reported for some dichalcogen dihalides. The molecular structure of disulfur dichloride in the gaseous state has been the subject of two electron diffraction studies (*36, 200*) and of two investigations by microwave spectroscopy (*282, 446*). Results are included in Table II.

In contrast to the monoselenium dihalides, the diselenium homologues Se_2Cl_2 and Se_2Br_2 are stable as pure liquids and solids, like the corresponding sulfur compounds S_2Cl_2 and S_2Br_2. They all could be characterized by full low-temperature structure analyses (*217, 232*). There are three crystal structure types, all containing Y–X–X–Y molecules with approximate C_2 symmetry and with dihedral angles between 83.9° and 87.4°. Bond lengths are shown in Table II. Different degrees of association of the molecules through X···X and X···Y contacts connect the molecules to layers and three-dimensional nets. The shortest contacts are S···Cl 3.375 Å in S_2Cl_2; S···S 3.482 Å (Se···Se 3.449 Å) in S_2Br_2 (α-Se_2Br_2); and Se···Br 3.373 Å (Se···Cl 3.319 Å) in β-Se_2Br_2 (Se_2Cl_2). In S_2Br_2 (α-Se_2Br_2) the association leads to interesting puckered chalcogen layers composed of X_6-rings with chair conformation. In β-Se_2Br_2 (Se_2Cl_2) the shortest contacts result in $(X_2Y_2)_2$ dimers with six-membered X_4Y_2 rings. These dimers can be detected from the appearance of a characteristic line at 215 cm^{-1} in low-temperature Raman spectra, the intensity of which was used to calculate the enthalpy of dimerization to be -17 kJ/mol (*416*).

B. HALO-CHALCOGENATES(II)

A novel class of chalcogen(II) halogen compounds was established recently by the preparation of the first simple binary mononuclear and oligomeric haloanions of divalent selenium and tellurium. The chemistry of these compounds is especially variable for selenium, and a number of highly interesting mono-, di-, tri, tetra- and pentanuclear anionic species with composition $X_nY_m^{2-}$ have been synthesized and characterized by structure analyses and spectroscopic studies up to now.

Tetrabromoselenate(II), $SeBr_4^{2-}$, and hexabromodiselenate(II), $Se_2Br_6^{2-}$, are formed as products in equilibrium mixtures of $SeOBr_2$ and/or $SeBr_4$ and their thermal reaction products in moderately polar organic solvents (*263, 372*); for example, according to

$$2SeOBr_2 \xrightarrow{70°C, CH_3CN} SeBr_4 + SeO_2(f) \tag{23}$$

$$SeBr_4 \longrightarrow SeBr_2 + Br_2;\ 2SeBr_4 \longrightarrow Se_2Br_2 + Br_2 \tag{24}$$

$$SeBr_2 + Br_2 + SeO_2 + 4RBr \xrightarrow{CH_3CN} R_2[SeBr_4] + R[SeO_2Br] + RBr_3 \tag{25}$$

$$2SeBr_2 + 2Br_2 + 4RBr \xrightarrow{70^\circ C,\ CH_3CN} R_2[Se_2Br_6] + 2RBr_3 \qquad (26)$$

(R is tetraalkylammonium, tetraarylphosphonium(arsonium), etc.)

1. *Mononuclear and Dinuclear Anions*

The square planar $SeBr_4^{2-}$anion in these orange-red salts is the prototype of the simple mononuclear type of halochalcogenates(II). Tetrachloroselenate(II), $SeCl_4^{2-}$, and the complete series of tetrahalotellurates(II), $TeCl_4^{2-}$, $TeBr_4^{2-}$, and TeI_4^{2-}, were obtained in this class by somewhat different preparative procedures (*172, 276, 371, 372*).

$SeCl_4^{2-}$ was synthetized in acetonitrile by reaction of Se and $SeCl_4$ (1 : 1), which equilibrate to solvated $SeCl_2$, and by subsequent nucleophilic addition of chlorides. Using large organosubstituted counter-cations to the chloride, the anion was crystallized as $[(HOC_2H_4)(C_6H_5)_3P]_2[SeCl_4] \cdot CH_3CN$ and as $[(C_6H_5)_3PNP(C_6H_5)_3]_2[SeCl_4] \cdot 2CH_3CN$ (*172, 276*).

For the synthesis of the tetrahalotellurates(II) (*371, 372*), which were isolated in crystalline form as light green to brown salts $[(C_6H_5)_4As]_2[TeCl_4]$, $[(C_6H_5)_4N]_2[TeBr_4] \cdot CH_3CN$, and $[(C_2H_5)_4N]_2[TeI_4]$, an excess of tellurium was reacted with halogen and halide according to

$$Te + Y_2 + 2\,Y^- \xrightarrow{CH_3CN} TeY_4^{2-} \qquad (Y = Cl, Br, I). \qquad (27)$$

In the initial phase of the heterogeneous reaction, TeY_6^{2-} is formed as an intermediate that comproportionates later according to

$$Te + TeY_6^{2-} + 2Y^- \rightarrow 2TeY_4^{2-} \qquad (28)$$

For the synthesis of $TeCl_4^{2-}$ this latter reaction with direct use of $TeCl_6^{2-}$ as starting material is preferable to the synthesis from the elements.

The structures of the mononuclear halochalcogenates(II) are square planar (ψ^2-octahedral) as predicted from VSEPR model considerations for these XY_4E_2 systems, which are isoelectronic to ICl_4^- or XeF_4. Their bond lengths (shown in Table III) are, as expected, somewhat larger than in the octahedral haloselenates(IV) and halotellurates(IV). Their bonding can be desribed as a system of two four-electron three-center bonds with a formal MO bond order of 0.5. As an example of one of the XY_4^{2-} species, the $SeBr_4^{2-}$ ion is shown together with the $Se_2Br_6^{2-}$ion in Fig. 27.

TABLE III

Se/Te-X BOND LENGTHS [Å] OF HALO-CHALCOGENATES(II) AND (IV)

X =	Cl	Br	I	Reference[a]
SeX_4^{2-}	2.441			*172, 276*
		2.598		*263*
SeX_6^{2-}	2.395			*405*
		2.565		*250*
TeX_4^{2-}	2.607			*371*
		2.753		*371*
			2.985	*371*
TeX_6^{2-}	2.541			*190*
		2.693		*60*
		2.701		*44*
			2.939	*218*

[a] Selected data.

The first reference to the existence of dinuclear haloselenates(II) was based on vibrational spectroscopic investigations (*439*). For the products obtained from the halogenating reactions of $[(C_2H_5)_4N]SeCN$ with $SeOCl_2$ or with bromine, an analytical Se : Cl(Br) ratio of 1 : 3 was observed in the resulting halo-anions. Planar dinuclear $Se_2Cl_6^{2-}$ and $Se_2Br_6^{2-}$ structures were correctly proposed for the products in the solid tetraethylammonium salts, in analogy to the known $[Se_2(SeCN)_6]^{2-}$ ion in $K[Se(SeCN)_3] \cdot \frac{1}{2}H_2O$ (*181*). From the vibrational spectra it was con-

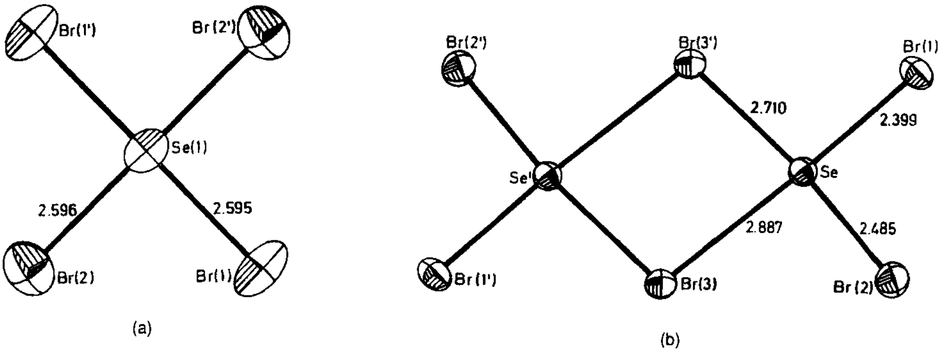


FIG. 27. Structures of (a) the $SeBr_4^{2-}$ and (b) the $Se_2Br_6^{2-}$ ions, both as analyzed in the tetraphenylphosphonium salts, with bond distances (Å) (*263*).

cluded that the dimers dissociate in solution and form discrete T-shaped trihaloselenates(II) $SeCl_3^-$ and $SeBr_3^-$ (*439*). A recent study of the Raman spectra of the reaction products of the systems $SeCl_2$/$[R_4N]Cl$ and $SeBr_2$/$[R_4N]Br$ in acetonitrile and in the solid (*295*), which is in accordance with similar independent studies (*21, 263, 276, 406*), gives a more detailed account of the vibrational spectra of the haloselenates(II) in solution. With increasing Cl^- (Br^-) concentration T-shaped mononuclear $SeCl_3^-$ ($SeBr_3^-$) and square planar $SeCl_4^{2-}$ ($SeBr_4^{2-}$) ions are formed. The chloro anions are less stable than the bromo anions; $SeCl_3^-$ is easily hydrolyzed to $SeOCl_3^-$, and it disproportionates in the laser beam to form $SeCl_6^{2-}$ and selenium. In the solid state the Raman spectra are consistent with the dinuclear $X_2Y_6^{2-}$ model for the 1 : 3 anions (*295*).

Full structural characterizations of the yellow hexachlorodiselenate(II) $Se_2Cl_6^{2-}$ and the orange-brown hexabromodiselenate(II) $Se_2Br_6^{2-}$ (Fig. 27) and proof of their identity were reported from the synthesis of the tetraphenylphosphonium salts. They were prepared, together with salts with various other large cations, and crystallized from the reaction of $SeCl_4$ with an excess of selenium and addition of $[(C_6H_5)_4P]Cl$ in dry CH_3CN (*172, 276*) or, respectively, from the system $SeOBr_2$/$[(C_6H_5)_4P]Br$/CH_3CN (see above) (*263, 372*).

The dinuclear planar $X_2Y_6^{2-}$ structure type of $Se_2Br_6^{2-}$ consists of two edge-sharing distorted XY_4 squares, and it is isoelectronic to I_2Cl_6 and isostructural, for example, to Au_2Cl_6 and Au_2Br_6. This structure was recently also observed in the novel homologous ion $Te_2I_6^{2-}$ (dark brown) as the tetraphenylphosphonium salt or with various other cations. $[(C_6H_5)_4P]_2[Te_2I_6]$ is formed as one of the products (besides $Te_2I_{10}^{2-}$) of the reaction of Te_4I_{16} with iodide in acetonitrile. Among the redox equilibria involved in this system the reaction

$$Te_2I_{10}^{2-} + 2I^- \rightleftharpoons Te_2I_6^{2-} + 2I_3^- \qquad (29)$$

is relevant for the formation of the $Te_2I_6^{2-}$ ion. Evidently the stability of the triiodide ion plays an important role for the course of the reaction (*107, 249*).

In all three planar hexahalo-dichalcogenate(II) anions $X_2Y_6^{2-}$, the bridging X–Y bond system in the central four-membered X_2Y_2 rings (for $Se_2Br_6^{2-}$; see Fig. 27), is strongly asymmetric, with $Se–Cl_{br}$ bond lengths of 2.620 and 2.739 Å in $Se_2Cl_6^{2-}$ and corresponding $Te–I_{br.}$ values of 3.061 and 3.215 Å in $Te_2I_6^{2-}$ (terminal bonds: Se–Cl, 2.291, 2.254 Å; Te–I, 2,853, 2.801 Å) (*107, 172, 249, 263, 276, 372*).

In the planar $X_2Y_6^{2-}$type halochalcogenates(II), the halogen ligands can be replaced by pseudo-halogens. The fully substituted derivatives $[Se_2(SCN)_6]^{2-}$ and $[Se_2(SeCN)_6]^{2-}$ in the salts $K[Se(XCN)_3 \cdot \frac{1}{2}H_2O$ (X = S, Se) have been known for some time, and their structures were determined (*181, 183*). Recently the successful synthesis of the first mixed-ligand derivative in this series was reported. The disubstituted bromothiocyanato anion $[Se_2Br_4(SCN)_2]^{2-}$ was prepared from $SeBr_2$ and $[(C_2H_5)_4N]SCN$ in CH_3CN (isolated as the tetraethylammonium salt) (*255, 256, 276*). In the centrosymmetric anion the S-bonded SCN ligands are perpendicular to the molecular plane in terminal *trans* positions.

It is interesting to note that the dihalo-pseudohalo-selenates(II) become mononuclear if the SCN^- and $SeCN^-$ ligands are replaced by cyanide. Dihalocyanoselenates(II) $SeCl_2CN^-$ and $SeBr_2CN^-$ have been synthesized by halogenation of tetraalkylammonium selenocyanate (a) with SO_2Cl_2 or with bromine (*439*) and (b) with phenylselenyl chloride or bromide according to (*48*)

$$[(CH_3)_4N]SeCN + 2C_6H_5SeY \rightarrow C_6H_5SeSeC_6H_5 + [(CH_3)_4N]SeY_2CN \quad \text{where } Y = Cl, Br \tag{30}$$

The $SeCl_2CN^-$ and $SeBr_2CN^-$ ions are monomeric, T-shaped, with almost linear symmetric Cl–Se–Cl and Br–Se–Br three-center bonds (Se–Cl 2.425 Å, Se–Br 2.575 Å). In *trans* position to the Se–C bond, Se has a close intermolecular contact to a nitrogen atom of a neighbouring CN group (Se···N 3.059, 3.172 Å). The coordination and bonding in the present XY_3E_2 systems can be described as a ψ^2-trigonal bipyramidal geometry with the stereochemically activated inert pairs (E) in equatorial positions, and with one 3c-4e Y–Se–Y bond plus one 2c-2e Se–C bond. From CNDO calculations the energies of the anions were computed as functions of the C–Se–Y angles. The minimum-energy geometries found agree well with the X-ray diffraction results (*48*).

2. *Tri-, Tetra-, and Pentanuclear Anions*

During attempts to prepare transition-metal derivatives of the haloselenates(II), the $Se_3Br_8{}^{2-}$ ion was obtained as the first trinuclear halochalcogenate(II) in 2-methyl-propionitrile solutions from $SeBr_4$, Se, and CuBr. It was isolated as the solvated copper(I) salt $[(i\text{-}C_3H_7CN)_4Cu]_2[Se_3Br_8]$ (*172, 255, 256, 276*). It has an unprecedented molecular structure, consisting of a triangular arrangement of three planar $SeBr_4$ groups sharing a common edge through two μ_3-bridging

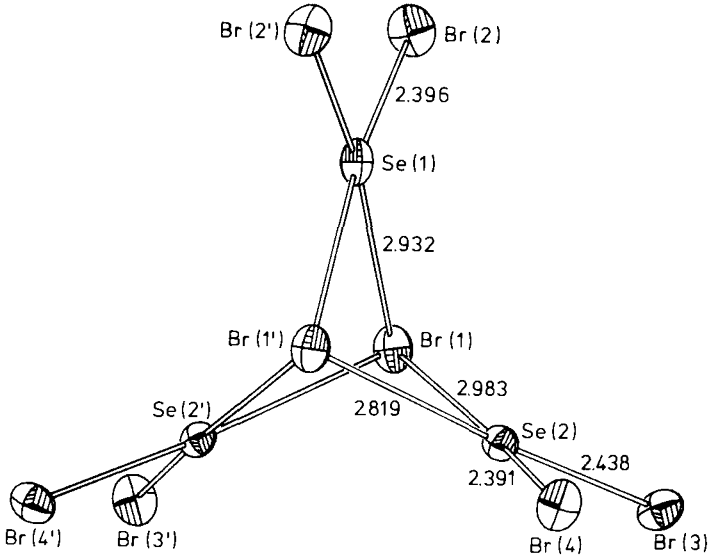


FIG. 28. Molecular structure of the $Se_3Br_8^{2-}$ anion, with bond lengths (Å) (*256*).

bromines. The anion is shown in Fig. 28. Its exact symmetry is C_2 with Se(1) on the twofold axis, the idealized symmetry being D_{3h}.

Another remarkable novel type of oligomeric molecular halochalcogenates with a tetranuclear framework and an unusual valence electron distribution and with linear halogen bridges has been reported recently. The first members of this type are $Se_4Br_{14}^{2-}$ and $Te_4I_{14}^{2-}$ (*107, 108, 185*). The dark-red-brown bromoselenate anion was prepared according to two different methods: (a) as $[(C_2H_5)(C_6H_5)_3P]_2[Se_4Br_{14}]$ from the reaction of 3 : 1 : 2 molar amounts of $SeBr_4$, Se, and ethyl-triphenyl-phosphonium bromide in dichloromethane (*108*), and (b) as $[(CH_3)_3(C_6H_5)N]_2[Se_4Br_{14}]$ by use of a modification of the known oxidation of selenocyanate by bromine (*181*). If Br_2 is used in excess together with additional Br^- in acetonitrile, $Se_4Br_{14}^{2-}$ is formed (*185*) in a multi-step redox reaction that can be summarized as

$$4Se(SeCN)_2 + 22Br_2 + 6Br^- \rightarrow 3Se_4Br_{14}^{2-} + 8BrCN \qquad (31)$$

$Te_4I_{14}^{2-}$ was synthesized as the black solvated Cu(I) salts $[Cu(RCN)_4]_2[Te_4I_{14}]$ with R = CH_3, C_2H_5, C_3H_7 from the redox equilibrium system of TeI_4 with CuI in acetonitrile at low CuI concentration (at higher concentrations TeI_6^{2-} is formed; see Section II,B) (*107, 108*). The overall redox reaction is summarized as

$$4TeI_4 + 2I^- \rightarrow Te_4I_{14}^{2-} + 2I_2 \qquad (32)$$

The mechanisms of these complex redox reactions during formation of the $X_4Y_{14}^{2-}$ moieties have yet to be explored.

In Fig. 29 the unit cell of $[Cu(C_3H_7CN)_4]_2[Te_4I_{14}]$ and the molecular

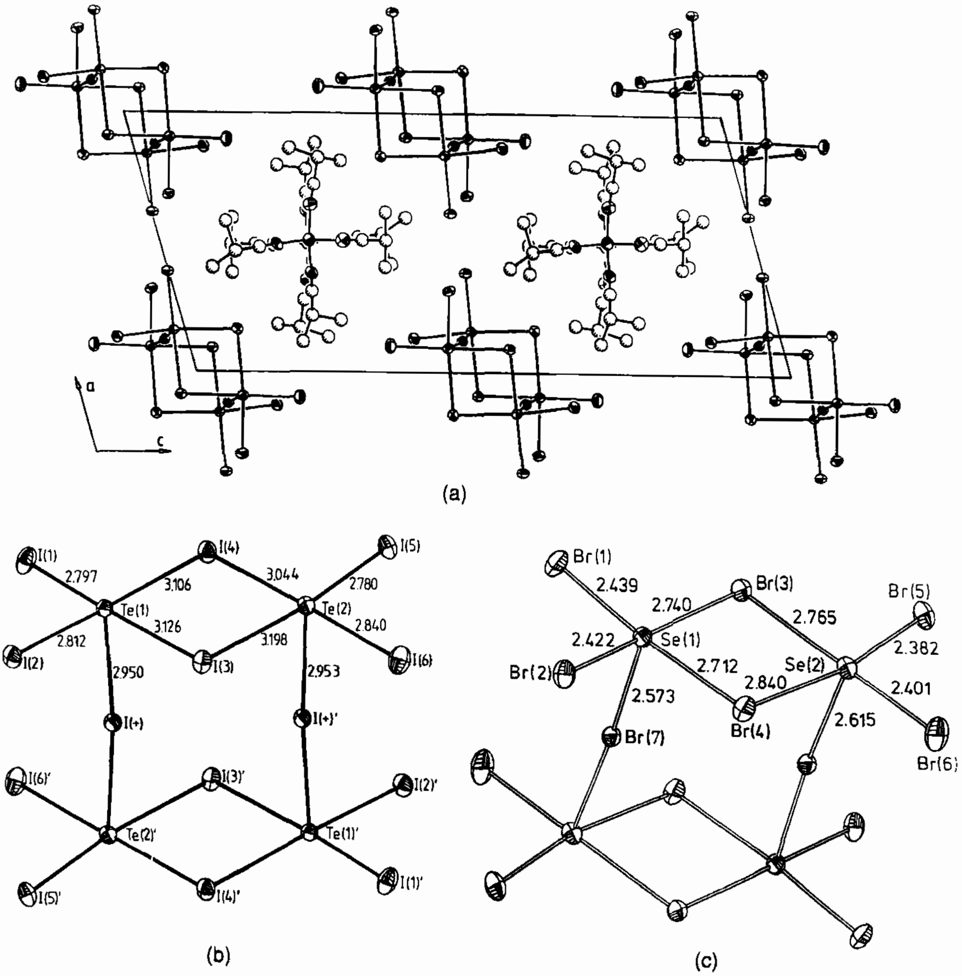


FIG. 29. (a) Unit cell of $[Cu(C_3H_7)_4]_2[Te_4I_{14}]$ and molecular structures of (b) $Te_4I_{14}^{2-}$ in (a) and of (c) $Se_4Br_{14}^{2-}$ in $[(C_2H_5)(C_6H_5)_3P]_2[Se_4Br_{14}]$, with bond lengths (Å) (*108, 185*).

structures of $Se_4Br_{14}^{2-}$ and $Te_4I_{14}^{2-}$ are shown (*107, 108;* see also *185*). In the tetranuclear molecules, planar dinuclear Se_2Br_6 and Te_2I_6 units very similar to the free $Se_2Br_6^{2-}$ and $Te_2I_6^{2-}$ ions (see above) are linked through two unusual linear Se–Br–Se resp. Te–I–Te bridges.

This symmetric di-μ-halobis-[di-μ-halobis(dihalochalcogenate)] structure can be tentatively rationalized (a) in a first step by assigning the formal oxidation numbers of +2 to the chalcogens, of +1 to the μ_2-bridging halogens with linear coordination, and of the usual −1 to all other halogen ligand atoms; and (b) in a second step in the interaction of the hypothetical Y^+ and $X_2Y_6^{2-}$ fragments via three-center four-electron bonds to form two linear X–Y–X bridges. The bonding model of three-center four-electron bonds, using only *p* orbitals of the chalcogens, can be applied to all linear Br–Se–Br (I–Te–I) and Se–Br–Se (Te–I–Te) fragments of the molecules. The 3c-4e bonds in the linear bridges leave nonbonding electron density in the *p*-lobes along the Y–X–Y axis, consistent with the accumulation of positive charge on the linearly coordinated halogens and with the absence of ligands *trans* to the linear bridges. The Se–Br–Se bond angles in $Se_4Br_{14}^{2-}$ are 175.9° (*185*) and 176.1° (*108*), the Te–I–Te angles in $Te_4I_{14}^{2-}$ are observed as 174.6° (*107, 108*). The bond distances (Fig. 29) in both homologous ions, with the values for the linear bridges being intermediate between the terminal bonds and those in the angular bridges, show very similar bonding in both $Se_4Br_{14}^{2-}$ and $Te_4I_{14}^{2-}$.

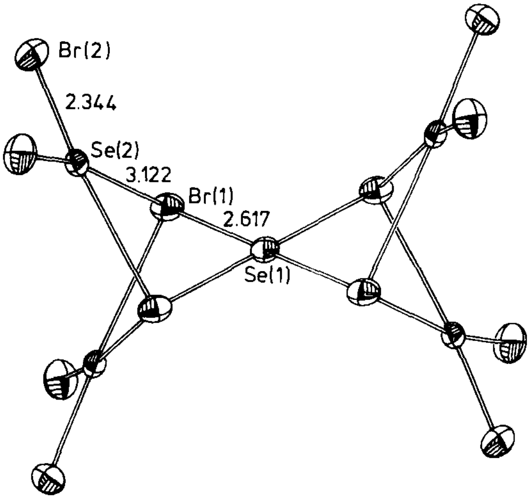


FIG. 30. $Se_5Br_{12}^{2-}$ ion in crystals of $[(C_3H_7)_4N]_2[Se_5Br_{12}]$, with bond distances (Å) (*21*).

If the reaction of selenium tetrabromide with selenium and bromides R^+Br^- is modified such that in the equilibrated reaction mixture the ratio of resulting $SeBr_2$ to R^+Br^- is more than 2.5, dodecabromopentaselenate(II) $Se_5Br_{12}^{2-}$ is formed (*21, 255, 256, 276*). It is the halochalcogenate(II) with the highest known degree of condensation, and it was isolated from solutions in CH_2Cl_2, for example, as the blackish-red tetrapropylammonium salt:

$$5SeBr_2 + 2[(C_3H_7)_4N]Br \rightarrow [(C_3H_7)_4N]_2[Se_5Br_{12}] \qquad (33)$$

The $Se_5Br_{12}^{2-}$ ion is shown in Fig. 30. It has D_{2h} symmetry and is composed of five planar $SeBr_4$ groups. Each of two pairs of two peripheral $SeBr_4$ groups share one edge with one another and with the central one; the two sharing edges of the central $SeBr_4$ square are in *trans* positions to each other (*21, 276*). The structure is related to the $Se_3Br_8^{2-}$ molecular ion (Fig. 28) (*172, 276*) from which it can be derived by addition of two more $SeBr_2$ molecules to a *trans* edge of one of the planar $SeBr_4$ groups. There are also structural relations between the $Se_5Br_{12}^{2-}$ ion and the polymeric structure of AuSeBr (*319*). The Se–Br bond lengths in the central $SeBr_4$ group (Fig. 30) are close to the values in the mononuclear $SeBr_4^{2-}$ ion (Fig. 27); the bridging Se–Br bonds from the peripheral groups to the μ_3-Br ligands are very long (Fig. 30). This bonding feature can be represented by the alternative structural formula $[(SeBr_4^{2-})(SeBr_2)_4]$.

C. Mixed-Valence Compounds

By further evaluation of the redox system $SeBr_4/SeBr_2/Se/Br^-$ in aprotic solvents (Section III,A), the first examples of bromoselenates(II,IV) containing selenium in both oxidation states +2 and +4 were prepared. Three dinuclear, trinuclear, and tetranuclear types of anions are reported in this novel class of mixed-valence compounds: $Se_2Br_8^{2-}$, $Se_3Br_{10}^{2-}$, and $Se_4Br_{12}^{2-}$. They are shown in Fig. 31. Similar to the bromoselenates(II), they were obtained by nucleophilic addition reactions of bromide ions within the complex reaction mixtures of selenium bromides. Evidently, the formation of Br_3^- is important for the stabilization of Se(II) in addition to Se(IV), shifting the equilibrium

$$\tfrac{1}{4}Se_4Br_{16} \rightleftharpoons SeBr_4 \rightleftharpoons SeBr_2 + Br_2 \qquad (34)$$

to the right and catalyzing the bromide transfer. Possible formal modes of reaction to the mixed valence anions are the addition of Br^- to $SeBr_4$

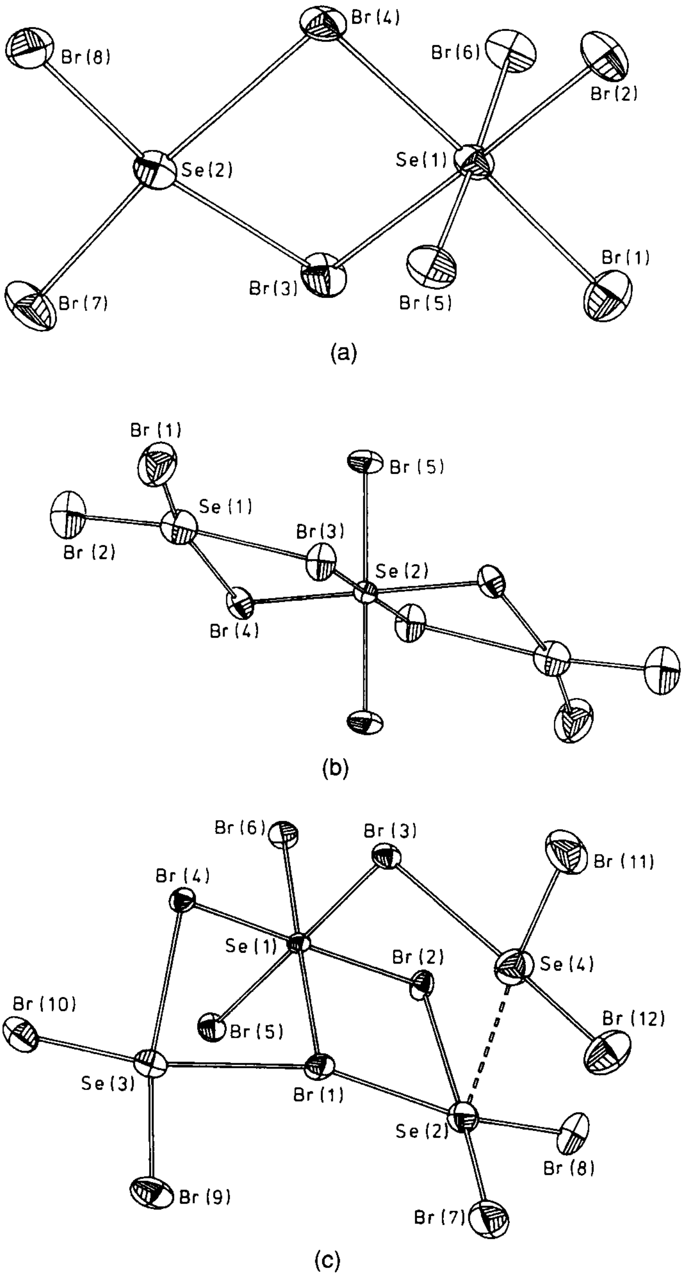


FIG. 31. Mixed-valence bromoselenate(II,IV) anions. (a) $[Se^{II}Se^{IV}Br_8]^{2-}$ in $[(C_2H_5)_4N]_2[Se_2Br_8]$, (b) $[Se^{II}_2Se^{IV}Br_{10}]^{2-}$ in $[(nC_3H_8)_4N]_2[Se_3Br_{10}]$, (c) $[Se^{II}_3Se^{IV}Br_{12}]^{2-}$ in $[(C_6H_5)_4P]_2[Se_4Br_{12}] \cdot CH_2Cl_2$, with important interatomic distances (Å) (*254*).

to give bromoselenates(IV) followed by addition of $SeBr_2$ molecules (or by the substitution of $SeBr_4$ groups by $SeBr_2$ groups) or, conversely, the addition of $SeBr_4$ to initially formed bromoselenates(II). The reproducible synthesis of pure products by crystallization was optimized by variation of composition, counter-ion, temperature, and solvent.

1. *Di-, Tri-, and Tetranuclear Anions*

Octabromodiselenate(II,IV) $[Se^{II}Se^{IV}Br_8]^{2-}$ was obtained by this method from CH_2Cl_2 as deep orange-red $[(C_2H_5)_4N]_2[Se_2Br_8]$ (*254–256*) and by an alternative method in a different crystal modification (*186*) by controlled oxidation of $Se(SeCN)_2$ with bromine according to the overall reaction

$$2Se(SeCN)_2 + 11Br_2 + 6Br^- \rightarrow 3Se_2Br_8^{2-} + 4BrCN \qquad (35)$$

In the anion an octahedral $Se^{IV}Br_6$ group shares one edge with a square planar $Se^{II}Br_4$ group. From the coordination, a clear assignment of the oxidation numbers is possible; the Se···Se distance is close to 4.0 Å, which excludes any bonding interactions. Surprisingly, the conformations of the $Se_2Br_8^{2-}$ moieties in the two crystal modifications differ significantly; the dihedral angles between the $Se^{II}Br_4$ plane and the basal plane of the $Se^{IV}Br_6$ octahedron is 34° (*254*) vs. 57° (*186*).

The reddish-black decabromotriselenate(II,IV) $[Se_2^{II}Se^{IV}Br_{10}]^{2-}$ was isolated as the *n*-propylammonium salt and derives from $Se_2Br_8^{2-}$ by addition of a second $SeBr_2$ moiety (*254*). In the centrosymmetric anion (Fig. 31) a central $Se^{IV}Br_6$ octahedron is linked through two *trans* edges to two square planar $Se^{II}Br_4$ groups with dihedral angles of 22° between the equatorial planes. The difference between bridging and terminal Se^{II}–Br bonds is even more pronounced than in $Se_2Br_8^{2-}$.

Dodecabromotetraselenate(II,IV) $[Se_3^{II}Se^{IV}Br_{12}]^{2-}$, crystallized as black-red $[(C_6H_5)_4P]_2[Se_4Br_{12}] \cdot CH_2Cl_2$ from solutions in CH_3CN/CH_2Cl_2, is the product of a variation of the reaction in the $SeBr_4/SeBr_2/Se/Br^-$ system. Its structure, as shown in Fig. 31, is particularly remarkable. Two $SeBr_2$ moieties are coordinated via *cis*-edges to the central $Se^{IV}Br_6$ octahedron. A third $SeBr_2$ moiety bridges one of the $Se^{IV}BrSe^{II}Br$ four-membered rings such that a short Se–Se distance of 3.335 Å results between Se(4) and Se(2) (see Fig. 31), indicating a weak bonding interaction. Se(2) thereby completes the square planar coordination geometry of Se(4). The $Se_4Br_{12}^{2-}$ ions are linked via unusually short intermolecular Br–Br contacts of 3.116 Å between Br(6) and Br(9), indicating strongly bonding charge-transfer interactions within a polymeric network.

The diamagnetic mixed-valence bromoselenates(II,IV) are to be assigned to class I in the Robin–Day scheme (*387*). Significant valence exchange is not to be expected, as concluded from the structural observations. The coordination geometries are clear indications of different selenium valences. The Se···Se distances are greater than 4 Å and thus rule out direct exchange contacts. Their colors differ little from those of pure Se(II) and Se(IV) analogues. UV/vis spectra have not yet been reported.

An especially interesting mixed-valence double salt was obtained from the equilibrium mixture in the redox system $Te/I_2/I^-$, which is described in Section III,B for the synthesis of TeI_4^{2-}. With benzyl-triethylammonium cations the compound $[(C_7H_7)(C_2H_5)_3N]_4[Te^{II}I_4][Te^{IV}I_6]$ could be crystallized, which contains the two kinds of mononuclear iodotellurate anions with different oxidation numbers (*107, 108*). The square planar TeI_4^{2-} ions (mean Te–I 2.956 Å) are connected to form layers through weak intermolecular I···I interactions (4.218 Å); a similar association to layers (I···I 4.191 Å) is observed for the slightly distorted TeI_6^{2-} octahedra (mean Te–I 2.925 Å). The unit cell is shown in Fig. 32.

2. *Cationic Species*

$Se_2Br_5^+$, as the first reported example of a novel dinuclear cationic halogen-chalcogen species (which is treated here, probably rather arbitrarily, under the heading of "mixed-valence compounds"), was prepared as the deep-purple crystalline hexafluoroarsenate from the following two different reactions in liquid SO_2 (*59, 321*):

$$4Se + 5Br_2 + 3AsF_5 \longrightarrow 2[Se_2Br_5^+][AsF_6^-] + AsF_3 \qquad (36)$$

$$[Se_4^+][AsF_6^-]_2 + 5Br_2 \longrightarrow 2[Se_2Br_5^+][AsF_6^-] \qquad (37)$$

The analogous reaction to (36) with I_2 leads to $[I_2SeSeSeSeI_2^{2+}]$-$[AsF_6^-]_2$ and not to the hypothetical $[Se_2I_5^+][AsF_6^-]$, as also supported by thermodynamic considerations (*321*). In the crystal structure of $[Se_2Br_5^+][AsF_6^-]$ the $Se_2Br_5^+$ cation, as shown in Fig. 33, consists of two trigonal pyramidal $SeBr_3$ units connected via a linear Se–Br–Se bridge. This interesting bonding situation, which is reminiscent of the linear bridges in $Se_4Br_{14}^{2-}$ and $Te_4I_{14}^{2-}$ (*107, 108, 185*) (see Section III,B) or in $[(S_7I)_2I^{3+}][SbF_6^-]_3$ (*354, 357*) (see Section IV), contains again, in an MO description, a linear 3c-4e Se–Br–Se bond. Here, the formally positive Br^+ links two $SeBr_2$ molecules (with formal oxidation number +2 for Se), the positive charge on Br being in accordance with

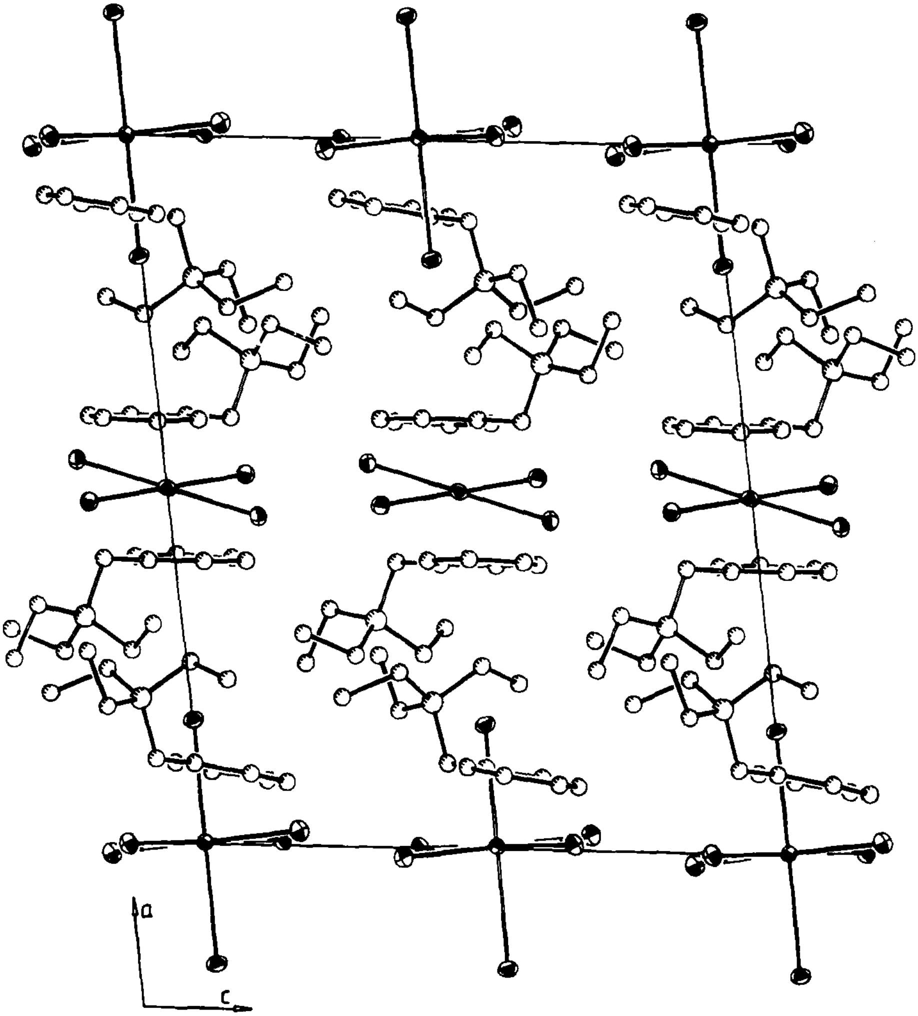


FIG. 32. Unit cell of the mixed-valence double salt $[(C_7H_7)(C_2H_5)_3N]_4[Te^{II}I_6][Te^{IV}I_6]$ *(249)*.

the localization of the two nonbonding electrons on the selenium atoms as postulated by the three-center bonding model. In an alternative VB approach the bonding is decribed employing the resonance structures $[Br_2Se^{(+)}\text{-}Br\ \ SeBr_2]$, $[Br_2Se\ \ Br\text{-}Se^{(+)}Br_2]$, and $[Br_2Se^{(+)}\text{-}Br^{(-)}\text{-}Se^{(+)}Br_2]$ *(321)*. The bridging bonds correspond to a bond order of 0.5. Selenium is linked through these secondary Se···F bonds of 2.98, 3.00, and 3.12 Å to the AsF_6^- ions in the crystal *(321)*.

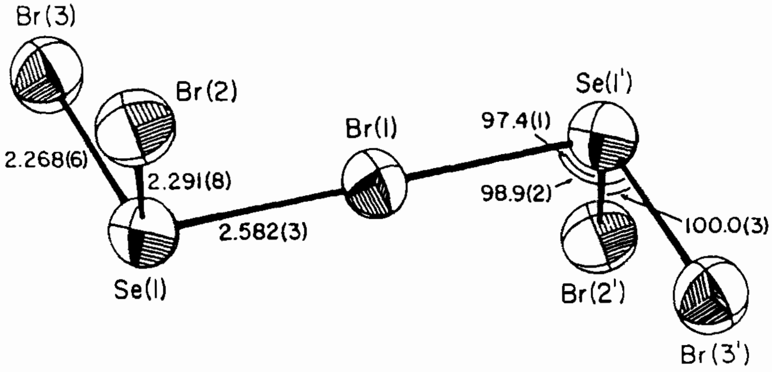


FIG. 33. Structure of the $Se_2Br_5^+$ cation in $[Se_2Br_5^+][AsF_6^-]$, with bond distances (Å) (*321*).

D. COMPLEXES WITH LEWIS BASES

A remarkable stabilization of selenium and tellurium dihalides is achieved if the central chalcogen atoms are coordinated with anionic (Section III,B) or with neutral Lewis bases as ligands. Thio ligands, especially thiourea and its substituted derivatives, have proven to be very efficient for this purpose, and many examples for stable square planar compounds of composition $Te(tu^*)_2Y_2$ and $[Te(tu^*)_4]^{2+}$ or, to a lesser extent, corresponding selenium analogues (tu* = unsubstituted or *N*-substituted thiourea, Y = Cl, Br, I, pseudo-halogen) are known (*124, 125, 127, 128, 132–138, 143;* for earlier work see *31, 126;* for corresponding Te(IV) complexes see *109, 131, 204*). The most straightforward way to their formation is the reaction of warm aqueous solutions of tellurium dioxide in HCl or HBr with those of the corresponding thiourea derivative. Depending on the molar proportions two series of compounds are formed:

$$Te^{IV} + 4tu^* + 2Y^- \longrightarrow Te^{II}(tu^*)_2Y_2 + [(tu^*)_2]^{2+} \quad (38)$$

$$Te^{IV} + 6tu^* \longrightarrow [Te^{II}(tu^*)_4]^{2+} + [(tu^*)_2]^{2+} \quad (39)$$

In these redox reactions, the thiourea reduces tellurium to Te(II) and is itself oxidized to formamidinium disulfide (*126*). The complexes are stable in the solid state as well as in acidic solutions and in organic solvents; in water they tend to hydrolyze with subsequent disproportionation of tellurium into Te(0) and Te(IV). The square planar complexes of the $Te(tu^*)_2Y_2$ type have normally the *cis* configuration, but *trans* isomers have also been prepared and characterized (*134, 137, 138*).

Also, analogous selenourea complexes of tellurium have been prepared (e.g., *126, 136, 138*). *cis*-Dichlorobis(thiourea)-selenium(II), $Se(tu)_2Cl_2$, and the homologous dibromo complex were prepared as the first compounds of this series with selenium as central atom (*50*).

By slight variation of the preparative methods, two types of dinuclear species in this series were obtained:

a. $Se_2(tmtu)_2Br_4$ (*445;* see also *443*), $Te_2(tmtu)_2Cl_4$, $Te_2(tmtu)_2Br_4$, and $Te_2(tmtu)_2I_4$ (*102, 131*) (tmtu is tetramethylthiourea) and their tetramethylselenourea (tmsu) analogues have planar $X_2S_2Y_4$ or $X_2Se_2Y_4$ frameworks (X = Se, Te; Y = Cl, Br, I) similar to the $Se_2Br_6^{2-}$ structure type (Section III,B), with selenium or tellurium in square planar coordination, with bridging halogen, and with the tmtu (tmsu) ligands in terminal positions (*102, 131, 445*).

b. In di-μ-bromobis[diethylenethioureatellurium(II)] dibromide, cationic $[Te_2(etu)_4Br_2]^{2+}$ molecules with the same planar structure of the $Te_2S_4Br_2$ framework and with the etu ligands in terminal positions were reported (*196*). Interestingly, in the corresponding ethyleneselenourea (esu) homologues two different isomers are observed: Whereas $[Te_2(esu)_4Br_2]^{2+}$ and $[Te_2(esu)_4I_2]^{2+}$ are isostructural to the sulfur-containing analogues, a second modification of $[Te_2(esu)_4Br_2]^{2+}$ and $[Te_2(esu)_4Cl_2]^{2+}$ have the esu molecules in bridging positions of the centrosymmetric dimer (*129*). These differences give some experimental evidence as to the relative coordinational *trans*-influence of Cl, Br, and I.

A compound with the composition $Te_7(etu)_{12}Br_{16}$ was found to have the structural formula $[Te_2(etu)_4Br_3{}^{+}]_3[Br^{-}][TeBr_6{}^{2-}]$ with a dinuclear bromine-bridged complex cation, which is shown in Fig. 34 (*140*); another one, with the composition $Te_3(trtu)_4Br_8$ (trtu = trimethylenethiourea), is *catena*-$[Te(trtu)_2Br^{+}]_{2n}[TeBr_6{}^{2-}]_n$ with planar *cis*-TeS_2Br_2 coordination groups joined via bromine bridges to form polymeric chains (*140*).

Examples for square planar complexes of Se(II) and Te(II) with other sulfur and selenium donor ligands such as thio- and selenocarbamates are given (e.g., in *29, 165, 205*). When triarylphosphane ligands were introduced as two-electron donors by the reaction of triarylphosphane selenide with Br_2, T-shaped Ar_3PSeBr_2 with the Br ligands in *trans* positions was prepared (*435*). Possibly, the molecules are dimerized via bromine bridges as in $Se_2(tmtu)_2Br_4$ (*445*).

As a final remark, a class of selenium(II) and tellurium(II) compounds should be mentioned that are another example of the strong

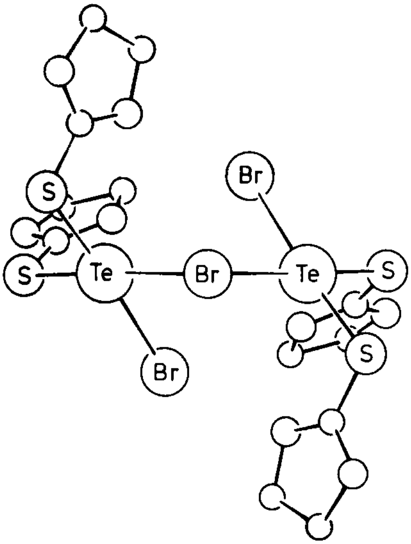


FIG. 34. View of the $[Te_2(etu)_4Br_3]^+$ cation in the crystal structure of $Te_7(etu)_{12}Br_{16}$ (*140*).

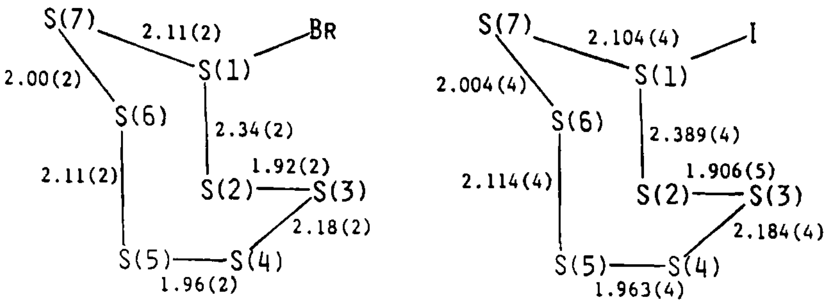
trans influence of organic groups as ligands. If aryl ligands are added to the mixed halogen/thiourea(selenourea) coordination of the chalcogen in compounds discussed in Section III,D, mononuclear, three-coordinate T-shaped species like $(C_6H_5)Te(su)Cl$ (*187*), $(C_6H_5)TeI_2^-$, and $(C_6H_5)TeIBr^-$ (*188, 226*), $(C_6H_5)SeBr_2^-$ (*444*), $(C_6H_5)Te(tmtu)Br$ (*189*) are formed (other examples: *130, 139, 184, 425, 426*). One nonbonding electron pair is to be assumed *trans* to the organic group; the tu* and/or halogen ligands are invariably *trans* to each other. An interesting variation of this geometry is realized in T-shaped 1,2,3-triselenetan-4-(Se,Se-dibromoselone), Se_3CSeBr_2, in which the coordination arond the central selenium is formed by two *trans* bromines and the four-membered C-bonded Se_3C ring (*269*).

IV. Chalcogen–Halogen Compounds with Homonuclear Chalcogen–Chalcogen Bonding

A. CATIONS CONTAINING HOMOATOMIC CHALCOGEN RINGS

Significant progress has been made in the chemistry of chalcogen-halogen compounds containing homoatomic chalcogen-chalcogen bonds ("chalcogen subhalides") on the molecular level as well as in solid state materials. A series of remarkable cationic sulfur–iodine, sulfur–bromine and selenium–iodine species have been prepared by various methods in strongly acidic media. $[S_7I^+][AsF_6^-]$ and $[S_7I^+][SbF_6^-]$ are obtained (a) from the reaction of excess sulfur and iodine with AsF_5 or SbF_5 in AsF_3; (b) by reaction of $S_x(AsF_6)_2$ (x ca. 19) with iodine in SO_2; (c) from $S_8(AsF_6)_2$ and KI in SO_2; or (d) by reaction of excess sulfur with I_3AsF_6 or with $I_2Sb_2F_{11}$ in SO_2 or in AsF_3 (*351, 360*). The S_7I^+ cation contains a seven-membered sulfur ring with a slightly twisted chair conformation similar to that of S_7. Together with the exocyclic iodine ligand, its molecular shape is similar to the structure of S_7O. The S–I bond length of 2.342 Å in $[S_7I^+][SbF_6^-]$ indicates a bond order of 1; the S–S distances vary from 1.906 to 2.389 Å; their characteristic alternating pattern (Fig. 35) can be explained by a superposition of the bond alternation in S_7 and that generated by the charged, three-coordinate S (*351*). If the reaction (a) above is varied with respect to solvent (SO_2) and stoichiometric ratio, the double salt $[S_7I^+]_4[S_4^{2+}][AsF_6^-]_6$ is obtained, also containing the novel iodo-cyclo-heptasulfur(1+) cation (*355, 357*). By synthetic paths similar to (a)–(d) above, the analogous bromo-cyclo-heptasulfur cation S_7Br^+ has been prepared in $[S_7Br^+][MF_6^-]$ (M = As, Sb) and in $[S_7Br^+]_4[S_4^{2+}][AsF_6^-]_6$ (*353*). The structural data of the univalent cation is shown in Fig. 35 in comparison to the S_7I^+ ion.

By a further variation of the synthetic procedure (a) described above, the bicyclic μ-iodo-bis(4-iodo-cyclo-heptasulfur)(3+) $(S_7I)_2I^{3+}$ cation was prepared in the compound $[(S_7I)_2I^{3+}][SbF_6^{6-}]_3 \cdot 2AsF_3$ (*354, 357*). Its molecular structure is shown in Fig. 36. It consists of two equivalent



(a) (b)

FIG. 35. (a) S_7Br^+ cation in $[S_7Br^+]_4[S_4^{2+}][AsF_6^-]_6$ and (b) S_7I^+ cation in $[S_7I^+][SbF_6^-]$, with bond lengths (Å) (*353, 360*).

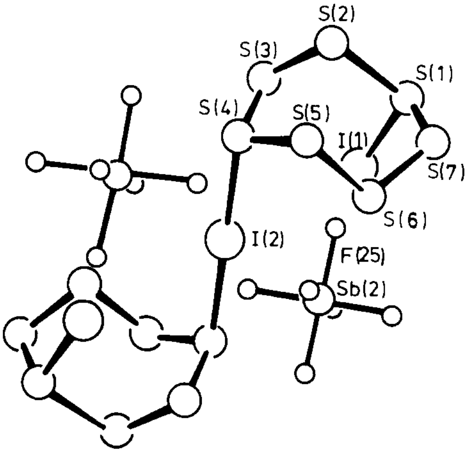


FIG. 36. Structure of $(S_7I)_2I^{3+}$ and two interacting SbF_6^- anions in crystalline $[(S_7I)_2I^{3+}][SbF_6^-]_3 \cdot 2AsF_3$ (*357*).

S_7I^+ units that are very similar to the iodo-cyclo-heptasulfur(1+) species reported above and that are linked via a linear iodine bridge at an inversion center. In addition to the linear I–S bonds (2.674 Å), the μ-iodine has a weak contact to each of the S_7I^+ units (S–I 3.777 Å) (*357*). The formal S–I bond order in the central linear S–I–S system is 0.5, and a positive charge has to be assumed on the central iodine, both in accordance with the 3c-4e bonding model.

An interesting type of polymeric homo-polyatomic cation closely related to the S_7I^+, S_7Br^+ and $(S_7I)_2I^{3+}$ species was obtained in the gold-colored $[Se_6I^+][AsF_6^-]$ (*328, 455*). It was prepared by two methods in liquid AsF_3

$$32Se + 2I_2 + 9AsF_5 \longrightarrow 4[Se_6I^+][AsF_6^-] + [Se_8^{2+}][AsF_6^-]_2 + 3AsF_3 \qquad (40)$$

$$12Se + I_2 + 3AsF_5 \longrightarrow 2[Se_6I^+][AsF_6^-] + AsF_3 \qquad (41)$$

and contains six-membered selenium rings with chair conformation that are connected via 1,4 axial selenium–iodine bonds to form polymeric $[Se_6I^+]_n$ ribbons. Again, the Se–I–Se bridges are linear with an assumed excess of positive charge on the iodine and with a comparatively weak bond (Se–I 2.736 Å) in accordance with the linear three-center MO model. A valence bond approach proposes the charges to be located more on the tricoordinate selenium according to the valence structures $\text{-I}\cdots\text{SeSe}_4\text{Se}^{(+)}\text{–I}\cdots\leftrightarrow\cdots\text{I–Se}^{(+)}\text{Se}_4\text{Se}\cdots\text{I-}$. Consistent with some charge delocalization into the ring, the Se–Se bonds adjacent to the Se–I bonds (mean 2.368 Å) are longer than the central Se–Se bonds (2.292 Å). There are weak intermolecular Se···Se (Fig. 37) and Se···I contacts (*328*). In a reaction similar to Eq. (40) above, a related cation, $Se_6I_2^{2+}$, also with a hexaselenium ring of chair conformation and with the two iodine ligands in axial 1,4 positions, was obtained in the compound $[Se_6I_2^{2+}][AsF_6^-]_2 \cdot 2SO_2$ (*361, 455*). Due to some positive charge delocalization into the ring, Se–Se bond alternation is observed. Each of the two iodine atoms makes two intra-ionic contacts (3.719 and 3.709 Å) with the dicoordinate Se atoms in the ring. The overall conformation of $Se_6I_2^{2+}$ is that of a distorted cube, and it has cluster-like characteristics (*361*).

The first example of a seven-membered selenium ring was reported recently in the Se_9Cl^+ cation of the novel compound $[Se_9Cl^+][SbCl_6^-]$ to be prepared by the reaction of selenium with $NOSbCl_6$ in SO_2 (*110*). The Se_9Cl^+ cation has a seven-membered selenium ring of chair conformation with an Se_2Cl chain endo-bonded to the 6 position of the ring. Short and long Se–Se bonds between 2.270 and 2.430 Å alternate in the ring, the longest one caused by repulsion of neighboring eclipsed lone pairs (as in S_7 rings).

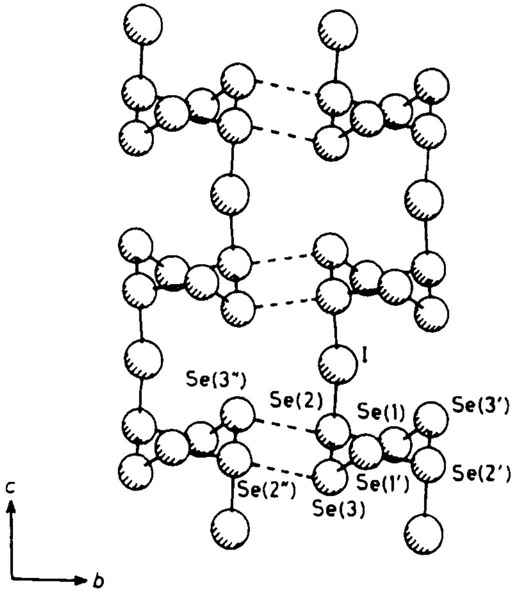


FIG. 37. The polymeric $[Se_6I^+]_n$ cations in crystalline $[Se_6I^+][AsF_6^-]$ (*328*).

B. ACYCLIC CATIONIC SYSTEMS

^{77}Se NMR spectroscopy was used to identify the novel $Se_4I_4^{2+}$ cation, which was synthesized by treating $[Se_4^{2+}][AsF_6^-]_2$ with I_2 in SO_2 (*69*). Its structure is proposed to be $[I_2Se^+SeSeSe^+I_2]$, and it is in equilibrium in solution with $Se_6I_2^{2+}$ and SeI_3^+.

$S_2I_4^{2+}$ and $Se_2I_4^{2+}$ have been reported recently as the first examples of a novel, interesting type of dichalcogen tetraiodine(2+) cations. They show remarkable differences in their structural and bonding pattern. $[S_2I_4^{2+}][AsF_6^-]_2$ is formed, besides AsF_3, by reaction of stoichiometric amounts of sulfur, iodine, and AsF_5 in liquid SO_2 (*352*). The $S_2I_4^{2+}$ cation as shown in Fig. 38 is distorted right triangular prismatic with a very short S–S distance of 1.828 Å (formal bond order 2.33) and two equal I–I bond distances of 2.597 Å (bond order 1.33). The structure is consistent with a +2/3 charge on each dimer unit and the essentially equal ionization potentials of S_2 and I_2 (*352*). The dimeric units are weakly bonded together by electrons in π^* orbitals, thus maximizing π bonding in each dimeric unit (*352*). $S_2I_4^{2+}$ is another example of a stable species containing homoatomic $3p\pi$-$3p\pi$ bonds as an exception to the conventional "double bond rule."

$Se_2I_4^{2+}$, which was synthesized according to the reaction

$$2[I_2^+][Sb_2F_{11}^-] + 2Se \xrightarrow{SO_2} [Se_2I_4^{2+}][Sb_2F_{11}^-]_2 \qquad (42)$$

has an eclipsed structure that only superficially resembles that of $S_2I_4^{2+}$ (*327*). It consists of two SeI_2^+ units connected by a very weak

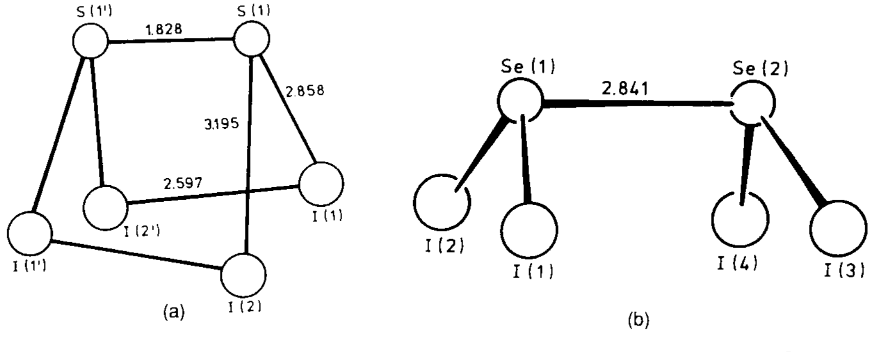


FIG. 38. Structures of (a) the $S_2I_4^{2+}$ cation in $[S_2I_4^{2+}][AsF_6^-]_2$ and (b) the $Se_2I_4^{2+}$ cation in $[Se_2I_4^{2+}][Sb_2F_{11}]_2$, with bond distances (Å) (*327, 352*).

Se–Se bond (Fig. 38). Its length is comparable to the transannular bond in Se_8^{2+}. The structure resembles that of the dithionite dianion, and, in a VB model, the weak central bond may be accounted for by the presence of positive charges on the adjacent Se atoms. If the $Se_2I_4^{2+}$ species is regarded as two SeI_2^+ radicals that are joined, in part, by overlap of the single electrons in each of the SeI_2^+ π^* MOs, bonding between all six atoms of the $Se_2I_4^{2+}$ unit results; the resulting formal Se–I bond order is 1.25 (*327*).

The most recent additions to the list of cationic products were obtained from reaction mixtures of chalcogen, halogen, and strong Lewis acids such as AsF_5 or SbF_5 in liquid SO_2 or AsF_3: the novel Br_2SSSBr^+ and $Br_2SeSeSeBr^+$ cations were obtained from such systems with hexafluoroarsenate as counter-ions (*358*). The structure of the $Br_2Se^+SeSeBr$ cation, which is very similar to the sulfur analogue, is shown in Fig. 39. The present Y_2X^+XXY cations are the simplest $X_nY_p^{q+}$ species (X = chalcogen, Y = univalent atom or group) in which bond alteration within a chain or ring of X atoms can occur, originating from a three-coordinate X^+. The Se–Se bond alternation of 0.34 Å is the largest so far observed in a selenium system. The high bond order of ca. 1.5 in the Se(2)–Se(3) bond of $Br_2Se^+SeSeBr$ indicates substantial

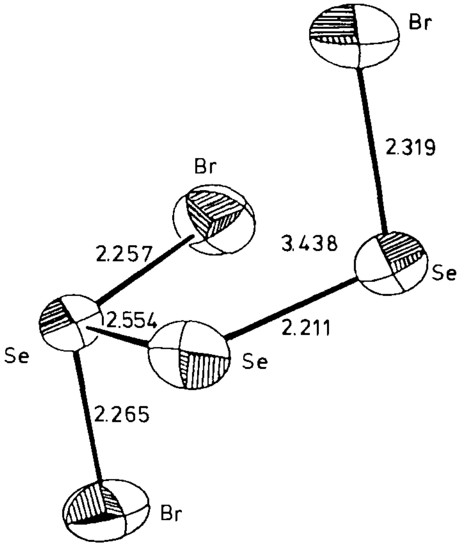


FIG. 39. Structure of the $Se_3Br_3^+$ cation in $[Br_2SeSeSeBr^+][AsF_6^-]$, with bond lengths (Å) (*358*).

$4p\pi$-$4p\pi$ bonding. It has been pointed out (*358*), that in this ability of polychalcogen halide cations and of homo-polyatomic cations of the halogens and chalcogens to form stable $np\pi$-$np\pi$ bonds ($n \geq 3$), they resemble second-row elements rather than other heavier elements that usually maximize σ-bond formation. In the $Br_2Se^+SeSeBr$ cation the Se atoms and one Br are coplanar; a weak interaction is to be assumed between Se(3) and this Br (Fig. 39) (Se–Br 3.438 Å). Evidently, the cluster-like structure maximizes the number of Se^+–Br bonds as well as Se–Se bond alternation, $p\pi$ bonding, and positive charge delocalization (*358*). There are only weak intermolecular secondary bonding contacts, the shortest being Se–Br 2.83 and 2.93 Å.

A somewhat different type of bonding is observed in the new compound (morpholinecarbodiselenoato)selenium(II) iodide, $[OC_4H_8NCSe_2Se]I$, in which selenium–selenium bonds are present and in which Se(II) is in a square planar coordination of 2 Se and 2 I. Polymeric ··Se···I···Se···I·· chains (Se–I 3.08–3.18 Å) are formed in the crystal (*46*).

C. SUBHALIDES OF TELLURIUM

The subhalides of tellurium are an especially important class of solid state compounds, and they have been the subject of intensive studies, so that a rather complete picture of their chemistry and their properties has been obtained in recent years. Because of their high tellurium content they contain fragments of the homonuclear tellurium chains; their "modified tellurium structures" are of great current interest with respect to possibly significant physical properties. Consequently, the results of various investigations on the synthesis of the compounds, on phase analysis by thermal methods, on crystal growth, on the structures, on spectroscopic, thermodynamic, optical, photoelectric, electrochemical properties have been reported in the last two decades. In a comprehensive review (*237*) all significant results are reported and discussed in detail so that the present chapter will be restricted to some selected and chemically important features.

From the phase diagrams of the quasi-binary systems Te–$TeCl_4$, Te–$TeBr_4$, and Te–TeI_4 the three thermodynamically stable incongruently melting subhalides Te_3Cl_2 (mp 239°C), Te_2Br (mp 225 °C), and α-TeI (mp 185°C) were identified and isolated in crystalline form (*71, 237, 238, 379*). In addition, two metastable subiodides, Te_2I and β-TeI, and a metastable subchloride, Te_2Cl, could be isolated as pure phases and characterized by different methods (*236, 237, 380*). A number of preparation methods are available for the dark-metallic to black subhalides:

a. Reaction of the elements under different elaborate conditions at well-defined temperatures of 200–300°C is followed by homogenization, annealing, quenching, or extraction of excess tellurium tetrahalide (*35, 379, 381*).

b. Te_2I, β-TeI, and α-TeI are obtained from hydrothermal syntheses at temperatures of ca. 200–280°C under isothermal or T-gradient conditions in concentrated aqueous hydroiodic acid (*236, 379–381*). This method is especially successful for growing single crystals.

c. Large crystals of the thermodynamically stable intermediate phases Te_3Cl_2, Te_2Br, and α-TeI are obtained from the melt by the Bridgman technique under conditions controlled by the phase diagram (*237*).

d. Solvent-free reactions in the redox systems TeY_4–SnY_2 (Y = Cl, Br, I) (*217, 218, 237*) lead to elemental Te for the chlorides, but form subbromides and subiodides according to

$$7SnBr_2 + 4TeBr_4 \longrightarrow 2Te_2Br + 7SnBr_4 \qquad (43)$$

$$3SnI_2 + 2TeI_4 \longrightarrow 2\alpha/\beta\text{-}TeI + 3SnI_4 \qquad (44)$$

As indicated in Fig. 40 the crystal structures of all six subhalides (*234–236, 381*) show remarkable relationships to the elemental tellurium chain structure. Te_3Cl_2 contains tellurium chains twisted around a 2_1 axis; every third Te atom has two chlorine ligands in axial positions *trans* to each other, resulting in a ψ-trigonal bipyramidal $Te(Cl_2Te_2E)$ (E: electron pair) coordination with local C_{2v} symmetry. In addition to the four intramolecular bonds, these Te atoms have two additional secondary intermolecular Te···Cl contacts at 3.363 and 3.400 Å (*234, 236, 381*). The three isotypic subhalides Te_2Cl, Te_2Br, and Te_2I can be described as chains of fused six-membered tellurium rings with boat conformation. They are bridged by halogen in such a way that every second Te atom gets a square-planar (ψ^2-octahedral) $Te(X_2Te_2E_2)$ coordination (*234, 236, 381*). The chains in β-TeI are closely related to those in the Te_2I structure (Fig. 40). They result if the double chains of Te_2I are cleaved along the central Te–Te bonds, and terminal iodine atoms are attached to the resulting free valences (*234–236, 380*). The crystal structure of α-TeI can be described as containing molecular Te_4I_4 units with a central four-membered tellurium ring. There are three different types of coordination around the tellurium atoms; the Te_4I_4 units are linked via short intermolecular Te···I contacts (Fig. 40) (*35, 234–236*).

Structure and bonding in the tellurium subhalides can be well rationalized, either employing valence and electron-counting rules, in-

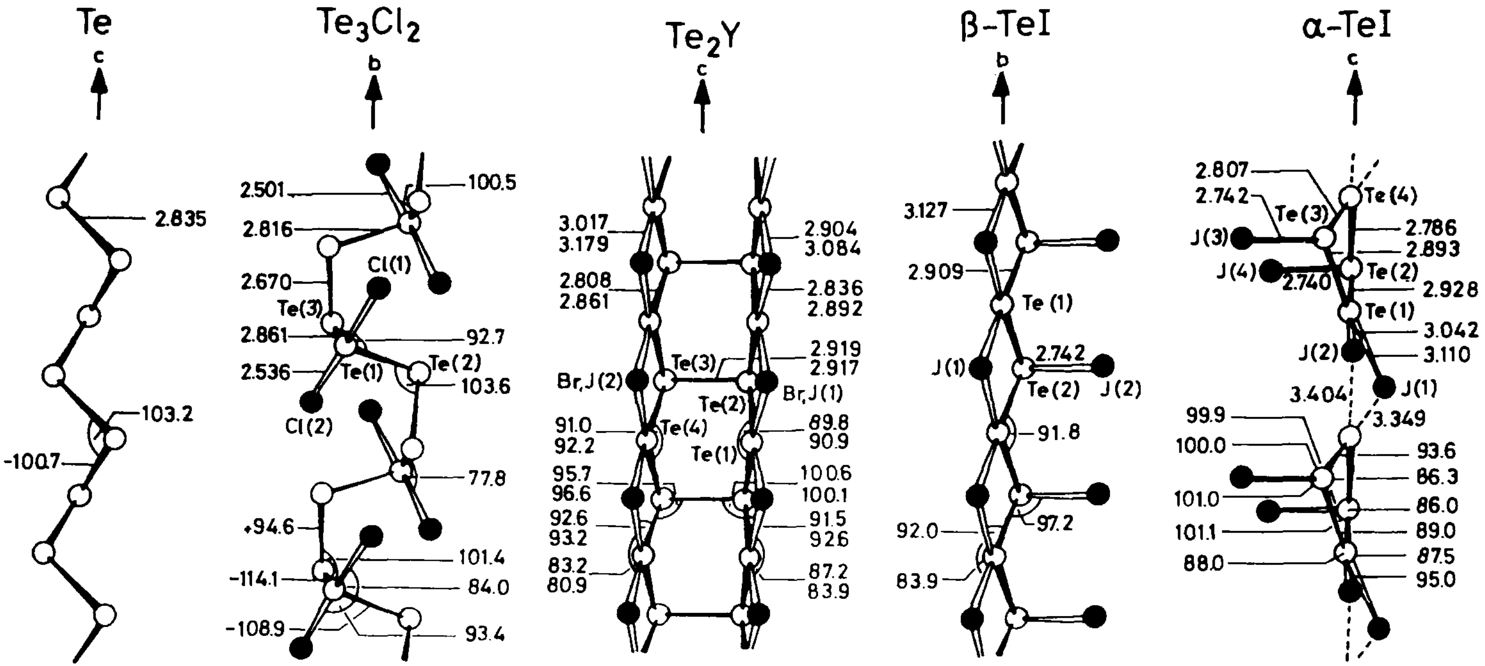


FIG. 40. Structural units of tellurium and tellurium subhalides ("modified tellurium structures") (*236, 237*). For the Te_2X structural type, the numbers above refer to Te_2Br and the numbers below refer to Te_2I. (○) Te and (●) Cl, Br, I. (*236*).

cluding the simple Gillespie–Nyholm model or more elaborate MO considerations using three-center bonding models in the linear three-atom fragments of the structures.

The interesting optical, electrical, and thermodynamic properties of the tellurium subhalides have been reviewed (*237*). They have larger band gaps and lower electrical conductivities than elemental tellurium. They have been found interesting and are being studied electrochemically (especially α-TeI) because of their possible use as solid electrolytes in galvanic cells (*237*).

Ternary subhalides $Te_2Br_{1-x}I_x$ were obtained as homogeneous glasses or, by annealing, as crystalline solid solutions that were investigated for their photoelectric properties by UV and X-ray photoemission experiments. ^{129}I Mössbauer spectra on polycrystalline α-TeI and ^{125}Te Mössbauer spectra of polycrystalline Te_3Cl_2, Te_2Br, Te_2I, β-TeI, and α-TeI, both at 4.2 K, have been reported and correlated with the crystal structures. Glasses in the systems Te–Cl and Te–Cl–S have been investigated in detail and proposed as a new class of infrared-transmitting materials (*274*).

An apparent additional tellurium-rich subiodide (*237*) was identified to be a novel type of intercalation compound with an idealized composition of $(Te_2)_2(I_2)$ and with a minimum experimental iodine content of $(Te_2)_2(I_2)_{0.42}$ (*227*). It consists of planar tellurium double layers with 1+4-coordination of the Te atoms, between which planar monomolelular layers of weakly associated I_2 molecules are intercalated.

As SeCl and α/β-SeBr are the only known subhalides of selenium and no binary compound exists in the Se–I system, the ternary system Se–Te–I was investigated. No distinct new phase is observed, but there is a region of intermediate solid solution α-$Te_{1-x}Se_xI$ with $x \leq 0.18$ (*228*).

V. Mixed Halides of Hexavalent Chalcogens

It has not been possible yet to prepare chalcogen(VI) hexahalides with the heavy halogens. The chemistry of hexavalent chalcogen compounds with bonds to chlorine, bromine, and iodine is essentially restricted to the mixed-ligand molecules $SClF_5$, $SBrF_5$, $SeClF_5$, $TeClF_5$, $TeBrF_5$, and derivatives thereof. By far the largest proportion of published papers refers to the sulfur compounds.

$SClF_5$ and $SBrF_5$ are important in organic synthesis because they add to a variety of olefins in a similar manner as the sulfenide halides, and a number of examples have been reported recently (for a review see *176, 277*). $SClF_5$ has been prepared from SF_4 and ClF with CsF as a catalyst (*401*). Precise structural data for $SClF_5$ have been obtained from electron diffraction and microwave data (S–Cl 2.045 Å, $S–F_{ax}$ 1.586 Å, $S–F_{eq}$ 1.564 Å) (*281*), which were compared with the results of CNDO/2 calculations (*272*). Raman and IR data in the solid state and in the matrix (*414*), including polarization data (*331*), as well as electron impact studies and appearance potentials (*178*) have been reported. Photochemical oxidation of $SClF_5$ was used to improve the synthesis of SF_5OOSF_5 (*437*). A high-yield synthesis of $SBrF_5$ involves the reaction of SF_4 with BrF_5 and Br_2 at 100°C/5 *d* (*290*), or of S_2F_{10} with a 10 : 1 excess of Br_2 at 150°C/16 *h* (*243*). Recent vibrational analyses and normal coordinate treatments on matrix, solid, liquid, and gaseous samples have been used to calculate force constants and thermodynamic data (*74, 414*).

$SeClF_5$ is prepared together with SeF_4 and Cl_2 from the reaction of SeF_4 with ClF at 350°C in an autoclave (*74, 400*) or in high yield from the reaction (*400*)

$$CsSeF_5 + ClSO_3F \rightarrow SeClF_5 + CsSO_3F \tag{45}$$

(see also *98, 158*). It is the first selenium(VI) compound with a stable Se–Cl bond, and it was characterized from its NMR and vibrational spectra as well as from thermochemical studies (*74*). From vibrational spectra a C_{4v} molecular symmetry was derived, and results of normal coordinate analyses and other bonding data, including results from SCF calculations (*163*), were reported (*33, 57, 74, 415*).

$TeClF_5$ and the rather unstable $TeBrF_5$ have been prepared in low yield by the reaction of F_2, diluted with N_2, with $TeCl_4$ or $TeBr_4$ at 25°C (*142*). Another convenient method condenses ClF onto TeF_4, $TeCl_4$, or TeO_2 and warms the reaction mixture to room temperature (*270*). From NMR spectra (*57*) and the analysis of the microwave spectrum (*271*) a C_{4v} structure was proposed, and from the vibrational spectrum a detailed normal coordinate analysis was undertaken (*57*). $TeClF_5$ is also formed if $TeBrF_5$ is reacted photochemically with Cl_2, which also converts PF_3 to PCl_2F_3 and $PClF_4$. Both $TeClF_5$ and $TeBrF_5$ undergo photochemical reactions with olefins at 25°C (*142*).

An interesting related compound, *trans*-$C_2F_5TeClF_4$, which is the first organic derivative of TeF_6 besides *trans*-$(C_2F_5)_2TeF_4$, has been reported to be formed if $(C_2F_5)_2Te_2$ or $C_2F_5TeCl_xF_{3-x}$ are reacted with ClF (*270*).

ACKNOWLEDGMENTS

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