

Table 16.7 Some physical properties of selenium oxohalides

Property	SeOF ₂	SeOCl ₂	SeOBr ₂	SeO ₂ F ₂	(SeOF ₄) ₂	F ₅ SeOF	F ₅ SeOOSF ₅
MP/°C	15	10.9	41.6	-99.5	-12	-54	-62.8
BP/°C	125	177.2	~220 (d)	-8.4	65	-29	76.3
Density/g cm ⁻³ (T°C)	2.80 (21.5°)	2.445 (16°)	3.38 (50°)	—	—	—	—

were noted for octahedral Sn^{II} (p. 380) and Sb^{III} (p. 568).

16.2.4 Oxohalides and pseudohalides⁽¹⁾

Numerous oxohalides of Se^{IV} and Se^{VI} are known, SeOF₂ and SeOCl₂ are colourless, fuming, volatile liquids, whereas SeOBr₂ is a rather less-stable orange solid which decomposes in air above 50° (Table 16.7). The compounds can be conveniently made by reacting SeO₂ with the appropriate tetrahalide and their molecular structure is probably pyramidal (like SOX₂, p. 694). SeOF₂ is an aggressive reagent which attacks glass, reacts violently with red phosphorus and with powdered SiO₂ and slowly with Si. In the solid state, X-ray studies have revealed that the pyramidal SeOF₂ units are linked by O and F bridges into layers thereby building a distorted octahedral environment around each Se with 3 close contacts (to O and 2F) and 3 (longer) bridging contacts grouped around the lone-pair to neighbouring units.⁽¹⁰⁹⁾ This contrasts with the discrete

molecular structure of SOF₂ and affords yet another example of the influence of preferred coordination number on the structure and physical properties of isovalent compounds, e.g. molecular BF₃ and 6-coordinate AlF₃, molecular GeF₄ and the 6-coordinate layer lattice of SnF₄ and, to a less extent, molecular AsF₃ and F-bridged SbF₃. (See also the Group 14 dioxides, etc.)

SeOCl₂ (Table 16.7) is a useful solvent: it has a high dielectric constant (46.2 at 20°), a high dipole moment (2.62 D in benzene) and an appreciable electrical conductivity (2 × 10⁻⁵ ohm⁻¹ cm⁻¹ at 25°). This last has been ascribed to self-ionic dissociation resulting from chloride-ion transfer: 2SeOCl₂ ⇌ SeOCl⁺ + SeOCl₃⁻.

Oxohalides of Se^{VI} are known only for fluorine (Table 16.7). SeO₂F₂ is a readily hydrolysable colourless gas which can be made by fluorinating SeO₃ with SeF₄ (or KBF₄ at 70°) or by reacting BaSeO₄ with HSO₃F under reflux at 50°. Its vibrational spectra imply a tetrahedral structure with C_{2v} symmetry as expected. By contrast, SeOF₄ is a dimer [F₄Se(μ-O)₂SeF₄] in which each Se achieves octahedral coordination via the 2 bridging O atoms: the planar central Se₂O₂ ring has Se-O 178 pm and angle Se-O-Se 97.5°, and Se-F_{eq} and Se-F_{ax} are 167 and 170 pm respectively.⁽¹¹⁰⁾

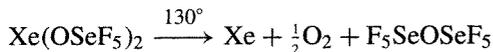
Two further oxofluorides of Se^{VI} can be prepared by reaction of SeO₂ with a mixture of F₂/N₂: at 80° the main product is the "hypofluorite" F₅SeOF whereas at 120° the peroxide F₅SeOOSeF₅ predominates. The compounds (Table 16.7) can be purified by

D. S. URCH, *J. Chem. Soc.* 5775-81 (1964); N. N. GREENWOOD and B. P. STRAUGHAN, *J. Chem. Soc. (A)* 962-4 (1966); T. C. GIBB, R. GREATREX, N. N. GREENWOOD and A. C. SARMA, *J. Chem. Soc. (A)* 212-17 (1970). J. D. DONALDSON, S. D. ROSS, J. SILVER and P. WATKISS, *J. Chem. Soc., Dalton Trans.*, 1980-3 (1975), and references therein. There is, however, some very recent X-ray crystallographic evidence that the anion in [Bu^tNH₃]₂⁺[TeBr₆]₂⁻ is trigonally distorted, with 3 long bonds of 276 pm (av.) and 3 shorter bonds of 261 pm, although the corresponding TeCl₆²⁻ salt had regular octahedral O_h symmetry: see L.-J. BAKER, C. E. F. RICKARD and M. J. TAYLOR, *Polyhedron* **14**, 401-5 (1995).

¹⁰⁹ J. C. DEWAN and A. J. EDWARDS, *J. Chem. Soc., Dalton Trans.*, 2433-5 (1976).

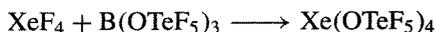
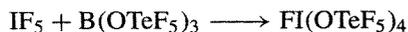
¹¹⁰ H. OBERHAMMER and K. SEPPALT, *Inorg. Chem.* **18**, 2226-9 (1979).

fractional sublimation and are reactive, volatile, colourless solids. The analogous sulfur compounds were discussed on p. 688. The colourless liquid $F_5SeOSeF_5$ (mp -85° , bp 53°) is made by a somewhat more esoteric route as follows:⁽¹¹¹⁾



The corresponding tellurium analogue, $F_5TeTeOF_5$, is made by fluorinating TeO_2 in a copper vessel at 60° using a stream of F_2/N_2 (1:10); it is a colourless, mobile, unreactive liquid, mp -36.6° bp 59.8° .^(76,77) The Se–O–Se angle in $F_5SeOSeF_5$ is 142.4° ($\pm 1.9^\circ$) as in the sulfur analogue, and the Te–O–Te angle is very similar ($145.5 \pm 2.1^\circ$). The fluorination of Te in the presence of oxygen yields (in addition to $Te_2F_{10}O$, p. 767) the dense colourless liquids $Te_3^{VI}O_2F_{14}$ and $Te_6^{VI}O_5F_{26}$. More purposeful synthetic routes have also been devised, leading to the isolation and structural characterization of the 6-coordinate Te^{VI} oxofluorides *cis*- and *trans*- $F_4Te(OTeF_5)_2$, *cis*- and *trans*- $F_2Te(OTeF_5)_4$, $FTe(OTeF_5)_5$ and even $Te(OTeF_5)_6$.⁽¹¹²⁾ Similarly, thermolysis of $B(OTeF_5)_3$ at 600° in a flow system yields the oxygen-bridged dimer $Te_2O_2F_8$ analogous to $Se_2O_2F_8$ above. $Te_2O_2F_8$ is a colourless liquid with a garlic-like smell, mp 28° , bp 77.5° . The planar central Te_2O_2 ring has Te–O 192 pm and angle Te–O–Te 99.5° , and again the equatorial Te–F distances (180 pm) are shorter than the axial ones (185 pm).⁽¹¹⁰⁾

The $-OTeF_5$ group (like the $-OSeF_5$ group) has a very high electronegativity as can be seen, for example, by the reactions of the ligand transfer reagent $[B(OTeF_5)_3]$:⁽¹¹³⁾



(see also p. 899)

Direct fluorination of $B(OTeF_5)_3$ at 115° gives a 95% yield of the hypofluorite, F_5TeOF , as a colourless gas which condenses to a colourless liquid below 0° and finally to a glass at about -80° ; the extrapolated bp is 0.6° .⁽¹¹⁴⁾ The chlorine derivative, $ClOTeF_5$, the so-called teflic acid, $HOTeF_5$, and the teflate anion, F_5TeO^- (as caesium or tetraalkylammonium salts) are also useful synthons for a variety of metal derivatives, e.g. $[Fe(OTeF_5)_3]$,⁽¹¹⁵⁾ $[Nb(OTeF_5)_6]^-$ and $[Ta(OTeF_5)_6]^-$.⁽¹¹⁶⁾ Other examples are $[Mn(CO)_5(OTeF_5)]$ and $[Pt(\text{norbornadiene})(OTeF_5)_2]$. The $-OTeF_5$ group can also act as a bridging ligand, as in the dimeric Ag^I and Tl^I complexes, $[\{(\eta^2\text{-tol})Ag\}_2(\mu\text{-}OTeF_5)_2]$ ⁽¹¹⁷⁾ and $[\{(\eta^6\text{-mes})_2Tl\}_2(\mu\text{-}OTeF_5)_2]$,⁽¹¹⁸⁾ which both feature a central planar M_2O_2 core (tol = toluene, C_6H_5Me ; mes = mesitylene, 1,3,5- $C_6H_3Me_3$). The H-bonded anion $[H(OTeF_5)_2]^-$ is also notable.⁽¹¹⁹⁾

Pseudohalides of Se in which the role of halogen is played by cyanide, thiocyanate or selenocyanate are known and, in the case of Se^{II} are much more stable with respect to disproportionation than are the halides themselves. Examples are $Se(CN)_2$, $Se_2(CN)_2$, $Se(SeCN)_2$, $Se(SCN)_2$, $Se_2(SCN)_2$. The selenocyanate ion $SeCN^-$ is ambidentate like the thiocyanate ion, etc., p. 325), being capable of ligating to metal centres via either N or Se, as in the osmium(IV) complexes $[OsCl_5(NCSe)]^{2-}$, $[OsCl_5(SeCN)]^{2-}$, and *trans*- $[OsCl_4(NCSe)(SeCN)]^{2-}$.⁽¹²⁰⁾ Tellurium and polonium pseudohalogen analogues include $Te(CN)_2$ and $Po(CN)_4$ but have been much

¹¹⁴ C. J. SCHACK and K. O. CHRISTE, *Inorg. Chem.* **23**, 2922 (1984).

¹¹⁵ T. DREWS and K. SEPELT, *Z. anorg. allg. Chem.* **606**, 201–7 (1991).

¹¹⁶ K. MOOCK and K. SEPELT, *Z. anorg. allg. Chem.* **561**, 132–8 (1988).

¹¹⁷ S. H. STRAUSS, N. D. NOIROT and O. P. ANDERSON, *Inorg. Chem.* **24**, 4307–11 (1985).

¹¹⁸ S. H. STRAUSS, N. D. NOIROT and O. P. ANDERSON, *Inorg. Chem.* **25**, 3851–3 (1986).

¹¹⁹ S. H. STRAUSS, K. D. ABNEY and O. P. ANDERSON, *Inorg. Chem.* **25**, 2806–12 (1986).

¹²⁰ W. PREETZ and U. SELLERBERG, *Z. anorg. allg. Chem.* **589**, 158–66 (1988).

¹¹¹ H. OBERHAMMER and K. SEPELT, *Inorg. Chem.* **17**, 1435–9 (1978).

¹¹² D. LENTZ, H. PRITZKOW and K. SEPELT, *Inorg. Chem.* **17**, 1926–31 (1978).

¹¹³ D. LENZ and K. SEPELT, *Angew. Chem. Int. Edn. Engl.* **17**, 355–6 and 356–61 (1978).

less studied than their Se counterparts. The long-sought tellurocyanate ion TeCN^- has finally been made, and isolated in crystalline form by the use of large counter-cations;⁽¹²¹⁾ as expected, the anion is essentially linear (angle $\text{Te}-\text{C}-\text{N}$ 175°), and the distances $\text{Te}-\text{C}$ and $\text{C}-\text{N}$ are 202 and 107 pm respectively.

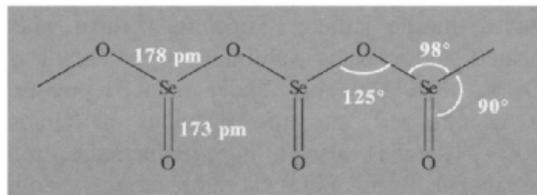
The selenohalides and tellurohalides of both main-group elements and transition metals have been compared with the corresponding thiohalides in two extensive reviews.⁽¹²²⁾ Other inorganic compounds of Se and Te, with bonds to N, P etc are described on pp. 783–6.

16.2.5 Oxides

The monoxides SeO and TeO have transient existence in flames but can not be isolated as stable solids. PoO has been obtained as a black, easily oxidized solid by the spontaneous radiolytic decomposition of the sulfoxide PoSO_3 .

The dioxides of all 3 elements are well established and can be obtained by direct

combination of the elements. SeO_2 is a white solid which melts in a sealed tube to a yellow liquid at 340° (sublimes at $315^\circ/760$ mmHg). It is very soluble in water to give selenous acid H_2SeO_3 from which it can be recovered by dehydration. It is also very soluble (as a trimer) in SeOCl_2 and in H_2SO_4 in which it behaves as a weak base. SeO_2 is thermodynamically less stable than either SO_2 or TeO_2 and is readily reduced to the elements by NH_3 , N_2H_4 or aqueous SO_2 (but not gaseous SO_2). It also finds use as an oxidizing agent in organic chemistry. In the solid state SeO_2 has a polymeric structure of corner-linked flattened $\{\text{SeO}_3\}$ pyramids each carrying a pendant terminal O atom:



TeO_2 is dimorphic: the yellow, orthorhombic mineral tellurite ($\beta\text{-TeO}_2$) has a layer structure in which pseudo-trigonal bipyramidal $\{\text{TeO}_4\}$ groups form edge-sharing pairs (Fig. 16.16a) which then further aggregate into layers (Fig. 16.16b) by sharing the remaining vertices. By contrast, synthetic $\alpha\text{-TeO}_2$ (“paratellurite”)

¹²¹ A. S. FOUST, *J. Chem. Soc., Chem. Commun.*, 414–5 (1979).

¹²² M. J. ATHERTON and J. H. HOLLOWAY, *Adv. Inorg. Chem. Radiochem.* **22**, 171–98 (1979). J. FENNER, A. RABENAU and G. TRAGESER, *Adv. Inorg. Chem. Radiochem.* **23**, 329–425 (1980).

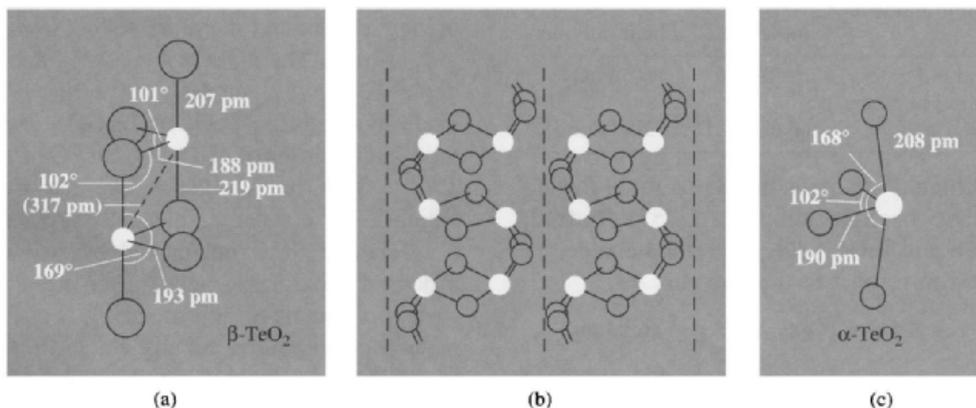


Figure 16.16 Structural units in crystalline TeO_2 : (a) pair of edge-sharing pseudo-trigonal bipyramidal $\{\text{TeO}_4\}$ groups in tellurite ($\beta\text{-TeO}_2$) which aggregate into layers as shown in (b) by sharing the remaining vertices with neighbouring pairs, and (c) the $\{\text{TeO}_4\}$ unit in paratellurite ($\alpha\text{-TeO}_2$).

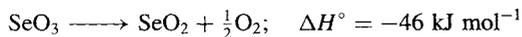
forms colourless tetragonal crystals in which very similar $\{\text{TeO}_4\}$ units (Fig. 16.16c) share all vertices (angle $\text{Te}-\text{O}-\text{Te}$ 140°) to form a rutile-like (p. 961) three-dimensional structure. TeO_2 melts to a red liquid at 733° and is much less volatile than SeO_2 . It can be prepared by the action of O_2 on Te , by dehydrating H_2TeO_3 or by thermal decomposition of the basic nitrate above 400° . TeO_2 is not very soluble in water; it is amphoteric and shows a minimum in solubility (at $\text{pH} \sim 4.0$). It is, however, very soluble in SeOCl_2 .

PoO_2 is obtained by direct combination of the elements at 250° or by thermal decomposition of polonium(IV) hydroxide, nitrate, sulfate or selenate. The yellow (low-temperature) fcc form has a fluorite lattice; it becomes brown when heated and can be sublimed in a stream of O_2 at 885° . However, under reduced pressure it decomposes into the elements at almost 500° . There is also a high-temperature, red, tetragonal form. PoO_2 is amphoteric, though appreciably more basic than TeO_2 : e.g. it forms the disulfate $\text{Po}(\text{SO}_4)_2$ for which no Te analogue is known.

It is instructive to note the progressive trend to higher coordination numbers in the Group 16 dioxides, and the consequent influence on structure:

Compound	SO_2	SeO_2
Coordination number	2	3
Structure	molecule	chain polymers
Compound	TeO_2	PoO_2
Coordination number	4	8
Structure	layer or 3D	3D "fluorite"

The difficulty of oxidizing Se to the +6 state has already been mentioned (p. 755). Indeed, unlike SO_3 and TeO_3 , SeO_3 is thermodynamically unstable with respect to the dioxide:

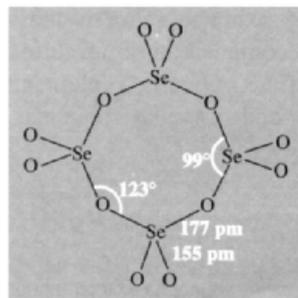


Some comparative figures for the standard heats of formation $-\Delta H_f^\circ$ are in Table 16.8. Accordingly, SeO_3 can not be made by direct oxidation of Se or SeO_2 and is even hard to make by the dehydration of H_2SeO_4 with P_2O_5 ; a better

Table 16.8 $-\Delta H_f^\circ$ (298)/ kJ mol^{-1} for MO_n from elements in standard states

SO_2	297	SeO_2	230	TeO_2	325
SO_3	432	SeO_3	184	TeO_3	348

route is to treat anhydrous K_2SeO_4 with SO_3 under reflux, followed by vacuum sublimation at 120° . SeO_3 is a white, hygroscopic solid which melts at 118° , sublimes readily above 100° (40 mmHg) and decomposes above 165° . The crystal structure is built up from cyclic tetramers, Se_4O_{12} , which have a configuration very similar to that of $(\text{PNCl}_2)_4$ (p. 538). In the vapour phase, however, there is some dissociation into the monomer. In the molten state SeO_3 is probably polymeric like the isoelectronic polymetaphosphate ions (p. 528).



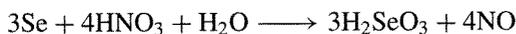
TeO_3 exists in two modifications. The yellow-orange α -form and the more stable, less reactive, grey β -form. The α - TeO_3 is made by dehydrating $\text{Te}(\text{OH})_6$ (p. 782) at 300 – 360° ; the β - TeO_3 is made by heating α - TeO_3 or $\text{Te}(\text{OH})_6$ in a sealed tube in the presence of H_2SO_4 and O_2 for 12 h at 350° . α - TeO_3 has a structure like that of FeF_3 , in which TeO_6 octahedra share all vertices to give a 3D lattice. It is unattacked by water, but is a powerful oxidizing agent when heated with a variety of metals or non-metals. It is also soluble in hot concentrated alkalis to form tellurates (p. 782). The β -form is even less reactive but can be cleaved with fused KOH .

PoO_3 may have been detected on a tracer scale but has not been characterized with weighable amounts of the element.

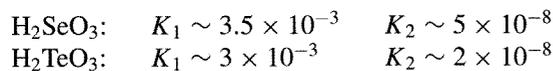
16.2.6 Hydroxides and oxoacids

The rich oxoacid chemistry of sulfur (pp. 705–21) is not paralleled by the heavier elements of the group. The redox relationships have already been summarized (p. 755). Apart from the dark-brown hydrated monoxide “Po(OH)₂”, which precipitates when alkali is added to a freshly prepared solution of Po(II), only compounds in the +4 and +6 oxidation states are known.

Selenous acid, O=Se(OH)₂, i.e. H₂SeO₃, and tellurous acid, H₂TeO₃, are white solids which can readily be dehydrated to the dioxide (e.g. in a stream of dry air). H₂SeO₃ is best prepared by slow crystallization of an aqueous solution of SeO₂ or by oxidation of powdered Se with dilute nitric acid:



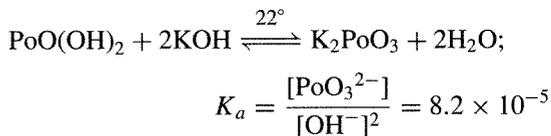
The less-stable H₂TeO₃ is obtained by hydrolysis of a tetrahalide or acidification of a cooled aqueous solution of a telluride. Crystalline H₂SeO₃ is built up of pyramidal SeO₃ groups (Se–O 174 pm) which are hydrogen-bonded to give an orthorhombic layer lattice. The detailed structure of H₂TeO₃ is unknown. Both acids form acid salts MHSeO₃ and MHTeO₃ by reaction of the appropriate aqueous alkali. The neutral salts M₂SeO₃ and M₂TeO₃ can be obtained similarly or by heating the metal oxide with the appropriate dioxide. Dissociation constants have not been precisely determined but approximate values are:



Alkali diselenites M₂Se₂O₅ are also known and appear (on the basis of vibrational spectroscopy) to contain the ion [O₂Se–O–SeO₂]²⁻, with C_{2v} symmetry and a nonlinear Se–O–Se bridge (cf. disulfite O₃S–SO₂²⁻, p. 720). Selenous acid, in contrast to H₂TeO₃, can readily be oxidized to H₂SeO₄ by ozone in strongly acid solution; it is reduced to elementary selenium by H₂S, SO₂ or aqueous iodide solution.

Hydrated polonium dioxide, PoO(OH)₂, is obtained as a pale-yellow flocculent precipitate by addition of dilute aqueous alkali to a solution

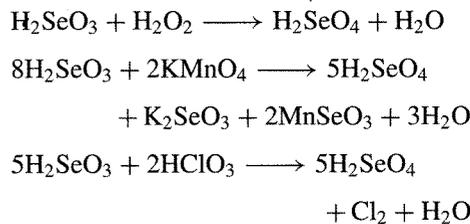
containing Po(IV). It is appreciably acidic, e.g.:



In the +6 oxidation state the oxoacids of Se and Te show little resemblance to each other. H₂SeO₄ resembles H₂SO₄ (p. 710) whereas orthotelluric acid Te(OH)₆ and polymetatelluric acid (H₂TeO₄)_n are quite different.

Anhydrous H₂SeO₄ is a viscous liquid which crystallizes to a white deliquescent solid (mp 62°). It loses water on being heated and combines readily with SeO₃ to give “pyroselenic acid”, H₂Se₂O₇ (mp 19°), and triselenic acid, H₄Se₃O₁₁ (mp 25°). It also resembles H₂SO₄ in forming several hydrates: H₂SeO₄·H₂O (mp 26°) and H₂SeO₄·4H₂O (52°). Crystalline H₂SeO₄ (*d* 2.961 g cm⁻³) comprises tetrahedral SeO₄ groups strongly H-bonded into layers through all 4 O atoms (Se–O 161 pm, O–H···O 261–268 pm). H₂SeO₄ can be prepared by several routes:

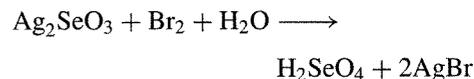
- (i) Oxidation of H₂SeO₃ with H₂O₂, KMnO₄ or HClO₃, which can be formally represented by the equations:



- (ii) Oxidation of Se with chlorine or bromine water, e.g.:

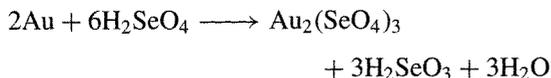


- (iii) Action of bromine water on a suspension of silver selenite:



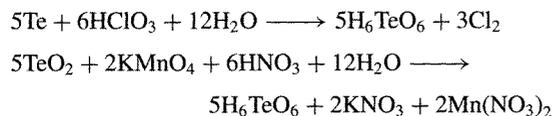
The acid dissociation constants of H₂SeO₄ are close to those of H₂SO₄, e.g. K₂ (H₂SeO₄)

1.2×10^{-2} . Selenates resemble sulfates and both acids form a series of alums (p. 76). Selenic acid differs from H_2SO_4 , however, in being a strong oxidizing agent: this is perhaps most dramatically shown by its ability to dissolve not only Ag (as does H_2SO_4) but also Au, Pd (and even Pt in the presence of Cl^-):

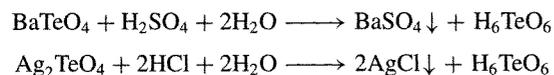


It oxidizes halide ions (except F^-) to free halogen. Solutions of S, Se, Te and Po in H_2SeO_4 are brightly coloured (cf. p. 664).

By contrast, the two main forms of telluric acid do not resemble H_2SO_4 and H_2SeO_4 and tellurates are not isomorphous with sulfates and selenates. Orthotelluric acid is a white solid, mp 136° , whose crystal structure is built up of regular octahedral molecules, $\text{Te}(\text{OH})_6$. This structure, which persists in solution (Raman spectrum), is also reflected in its chemistry; e.g. breaks occur in the neutralization curve at points corresponding to NaH_5TeO_6 , $\text{Na}_2\text{H}_4\text{TeO}_6$, $\text{Na}_4\text{H}_2\text{TeO}_6$ and Na_6TeO_6 . Similar salts include Ag_6TeO_6 and Hg_3TeO_6 . Moreover diazomethane converts it to the hexamethyl ester $\text{Te}(\text{OMe})_6$. In this respect Te resembles its horizontal neighbours in the periodic table Sn, Sb and I which form the isoelectronic species $[\text{Sn}(\text{OH})_6]^{2-}$, $[\text{Sb}(\text{OH})_6]^-$ and $\text{IO}(\text{OH})_5$. Orthotelluric acid can be prepared by oxidation of powdered Te with chloric acid solution or oxidation of TeO_2 with permanganate in nitric acid:

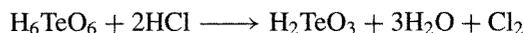


Alternatively, Te or TeO_2 can be oxidized by $\text{CrO}_3/\text{HNO}_3$ or by 30% H_2O_2 under reflux. Acidification of a tellurate with an appropriate precipitating acid offers a further convenient route:



Crystallization from aqueous solutions below 10° gives the tetrahydrate $\text{H}_6\text{TeO}_6 \cdot 4\text{H}_2\text{O}$. The

anhydrous acid is stable in air at 100° but above 120° gradually loses water to give polymetateuric acid and allotelluric acid (see below). Unlike H_2SO_4 and H_2SeO_4 , H_6TeO_6 is a weak acid, approximate values of its successive dissociation constants being $K_1 \sim 2 \times 10^{-8}$, $K_2 \sim 10^{-11}$, $K_3 \sim 3 \times 10^{-15}$. It is a fairly strong oxidant, being reduced to the element by SO_2 and to H_2TeO_3 in hot HCl:



Polymetateuric acid $(\text{H}_2\text{TeO}_4)_{\sim 10}$ is a white, amorphous hygroscopic powder formed by incomplete dehydration of H_6TeO_6 in air at 160° . Alternatively, in aqueous solution the equilibrium $n\text{H}_6\text{TeO}_6 \rightleftharpoons (\text{H}_2\text{TeO}_4)_n + 2n\text{H}_2\text{O}$ can be shifted to the right by increasing the temperature; rapid cooling then precipitates the sparingly soluble polymetateuric acid. The structure is unknown but appears to contain 6-coordinate Te. Allotelluric acid " $(\text{H}_2\text{TeO}_4)_3(\text{H}_2\text{O})_4$ " is an acid syrup obtained by heating $\text{Te}(\text{OH})_6$ in a sealed tube at 305° : the compound has not been obtained pure but tends to revert to H_6TeO_6 at room temperature or to $(\text{H}_2\text{TeO}_4)_n$ when heated in air; indeed, it may well be a mixture of these two substances.

Tellurates are prepared by fusing a tellurite with a corresponding nitrate, by oxidizing a tellurite with chlorine, by or neutralizing telluric acid with a hydroxide.⁽¹²³⁾ An interesting variant is to heat intimate mixtures of TeO_3 with metal oxides. For example, with Rb_2O at 680° for several weeks, colourless crystals having the unusual stoichiometry $\text{Rb}_6\text{Te}_2^{\text{VI}}\text{O}_9$ were formed which contained both tetrahedral TeO_4^{2-} and trigonal bipyramidal TeO_5^{4-} groups, i.e. $\text{Rb}_6[\text{TeO}_5][\text{TeO}_4]$.⁽¹²⁴⁾

Numerous peroxyacid or thioacid derivatives of Se and Te have been reported⁽¹⁾ but these add little to the discussion of the reaction chemistry or the structure types already

¹²³ Ref. 11, pp. 94–7.

¹²⁴ T. WISSER and R. HOPPE, *Z. anorg. allg. Chem.* **584**, 105–13 (1990).

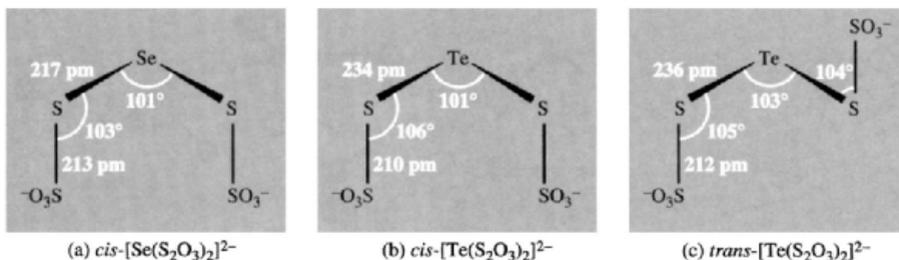


Figure 16.17 Structures and conformations of unbranched chain anions in (a) Ba[Se(S₂O₃)₂].2H₂O, (b) Ba[Te(S₂O₃)₂].2H₂O, and (c) (NH₄)₂[Te(S₂O₃)₂].

described. Examples are peroxoselenous acid HOSeO(OOH) (stable at -10°) and potassium peroxy-orthotellurate K₂H₄TeO₇ which also loses oxygen at room temperature. Isomeric selenosulfates, M₂S₂O₃Se, and thioselenates, M₂SeO₃S, are known and can be made by the obvious routes of [SO₃²⁻(aq) + Se] and [SeO₃²⁻(aq) + S]. Likewise, colourless or yellow-green crystalline selenopolythionates M₂Se_xS_yO₆ ($x = 1, 2; y = 2, 4$) and orange-yellow telluropentathionates M₂TeS₄O₆ are known. X-ray structure analysis reveals unbranched chains with various conformations as found for the polythionates themselves (p. 718).⁽¹²⁵⁾ Typical examples are in Fig. 16.17. It will be seen that these compounds contain Se and Te bonded to S rather than O and they therefore form a natural link with the Group 16 sulfides to be described in the next section.

16.2.7 Other inorganic compounds

The red compound Se₄S₄, obtained by fusing equimolar amounts of the elements, is a covalent molecular species which can be crystallized from benzene. Similar procedures yield Se₂S₆, SeS₇ and TeS₇, all of which are structurally related to S₈ (p. 654; see also p. 763).

PoS forms as a black precipitate when H₂S is added to acidic solutions of polonium compounds. Its solubility product is $\sim 5 \times 10^{-29}$. The

action of aqueous ammonium sulfide on polonium(IV) hydroxide gives the same compound. It decomposes to the elements when heated to 275° under reduced pressure and is of unknown structure.

The chemistry of compounds containing Se–N and Te–N bonds has been very actively developed during the past decade and many new and unusual species are emerging.^(126,127) Se₄N₄ is an orange, shock sensitive crystalline compound which decomposes violently at 160°. It resembles its sulfur analogue (p. 722) in being thermochroic (yellow-orange at -195° , red at $+100^\circ$) and in having the same *D*_{2d} molecular structure. Se₄N₄ can be made by reacting anhydrous NH₃ with SeBr₄ (or with SeO₂ at 70° under pressure). A new red-brown crystalline modification, β-Se₄N₄, which has a very similar cluster structure but differs in the packing arrangement, has recently been prepared by reacting SeO₂ with the phosphane imine, Me₃SiNPM₃.⁽¹²⁸⁾ Tellurium nitride can be prepared similarly (TeBr₄ + NH₃); it is a lemon-yellow, violently explosive compound with a formula that might be Te₃N₄ rather than Te₄N₄; its structure is unknown.

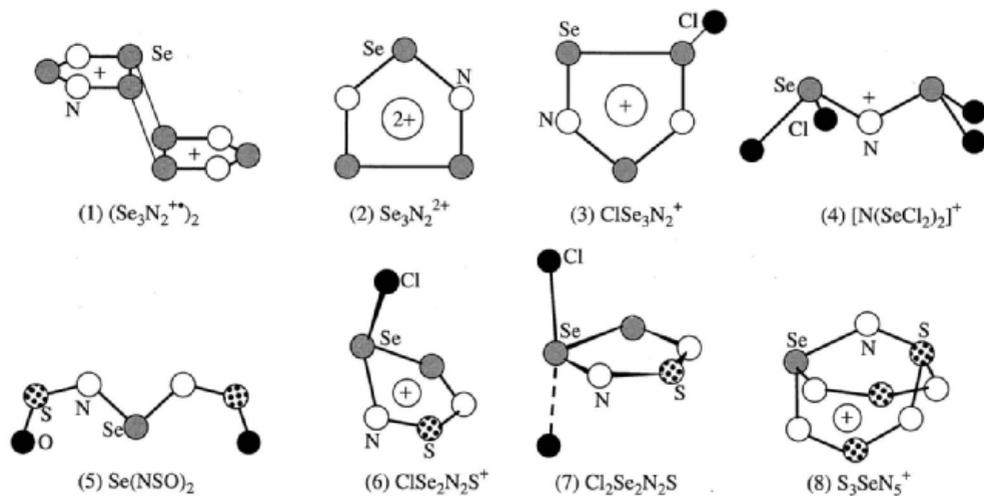
Se₄N₄ reacts with [PtCl₂(PMe₂Ph)₂] in liquid ammonia (50 atm.) to give a quantitative yield of [Pt(η²-Se₂N₂)(PMe₂Ph)₂] which features a

¹²⁶ M. BJÖRGVINSSON and H. W. ROESKY, *Polyhedron* **10**, 2353–70 (1991).

¹²⁷ P. F. KELLY, A. M. Z. SLAWIN, D. J. WILLIAMS and J. D. WOOLLINS, *Chem. Soc. Rev.* **21**, 245–52 (1992). T. M. KLAPÖTKE, in R. STEUDEL (ed.), *The Chemistry of Inorganic Ring Systems*, Elsevier, Amsterdam, 1992, pp. 409–27.

¹²⁸ H. FOLKERTS, B. NEUMÜLLER and K. DEHNICKE, *Z. anorg. allg. Chem.* **620**, 1011–15 (1994).

¹²⁵ A. F. WELLS, *Structural Inorganic Chemistry*, 5th edn., pp. 726–35, Oxford University Press, Oxford, 1984. See also *J. Chem. Soc., Dalton Trans.*, 1528–32 (1978) (Pb₂Te₃O₈). *Inorg. Chem.* **19**, 1040–3, 1044–8, 1063–4 (1980) (SeS₃O₆²⁻, Se₂S₂O₆²⁻, SeS₂O₆²⁻).



5-membered $\overline{\text{Pt-SeNSeN}}$ heterocycle at the planar Pt centre.⁽¹²⁹⁾ A similar reaction with $[\text{Pt}(\text{PPh}_3)_3]$ in CH_2Cl_2 gives the analogous PPh_3 complex plus the related dark-green dimer, $[(\text{Ph}_3\text{P})\text{Pt}(\mu, \eta^2\text{-Se}_2\text{N}_2)_2\text{Pt}(\text{PPh}_3)]$, in which the chelating ligand also bridges the two Pt atoms via the ipso-N atoms so as to form a central planar Pt_2N_2 core which is also coplanar with the two planar 5-membered heterocycles.⁽¹³⁰⁾ Innumerable other Se/N species have been synthesized and characterized by X-ray diffraction analysis, e.g. the 7π -electron radical cation $\text{Se}_3\text{N}_2^{\cdot+}$ (1),⁽¹³¹⁾ the 6π -electron dication $\text{Se}_3\text{N}_2^{2+}$ (2),⁽¹³¹⁾ ClSe_3N_2 (3),⁽¹³²⁾ $[\text{N}(\text{SeCl}_2)_2]^+$ (4),⁽¹³³⁾ $\text{Se}(\text{NSO})_2$ (5),⁽¹³⁴⁾ $\text{ClSe}_3\text{N}_2\text{S}^+$ (6),⁽¹³⁴⁾ $\text{Cl}_2\text{Se}_2\text{N}_2\text{S}$ (7),⁽¹³⁴⁾ $[\text{S}_3\text{SeN}_5]^+$ (8),⁽¹³⁴⁾ etc. The original papers should be consulted for preparative procedures.

Metal complexes with Se/N ligands are also appearing in increasing numbers in the literature. Thus, *cyclo*- Se_4N_2 forms the red-brown donor-acceptor complexes $[\text{SnCl}_4(\eta^1\text{-N}_2\text{Se}_4)_2]$ (9) and $[\text{TiCl}_4(\eta^2\text{-N}_2\text{Se}_4)]$,⁽¹³⁵⁾ whereas reaction of $[\text{Se}_2\text{SN}_2]_2\text{Cl}_2$ with *cis*- $[\text{PtCl}_2(\text{PMe}_2\text{Ph})_2]$ in liquid ammonia gives $[\text{Pt}(\eta^2\text{-SeSN}_2)(\text{PMe}_2\text{Ph})_2]$ which in turn can be protonated with HBF_4 to give $[\text{Pt}(\eta^2\text{-SeSN}_2\text{H})(\text{PMe}_2\text{Ph})_2]^+$ (10).⁽¹³⁶⁾ The di-Se analogues with $\eta^2\text{-Se}_2\text{N}_2^{2-}$ and $\eta^2\text{-Se}_2\text{N}_2\text{H}^-$ have also been characterized.⁽¹³⁷⁾

Heterocycles involving P^{V} include $[1,5\text{-}(\text{Ph}_2\text{P})_2\text{N}_4(\text{SeMe})_2]$ (11), which has an 8-membered chair configuration with the two Se atoms displaced on either side of the P_2N_4 plane, and the related $[1,5\text{-}(\text{Ph}_2\text{P})_2\text{N}_4\text{Se}_2]$ (12).⁽¹³⁸⁾ The reaction of (12) with $[\text{PtCl}_2(\text{PEt}_3)_2]$ gives the η^1 -complexes (13), (14) which, in turn, can be oxidatively added to $[\text{Pt}(\eta^2\text{-C}_2\text{H}_4)(\text{PPh}_3)_2]$ to give the $\eta^2\text{-Se,Se}'$ complexes (15) and (16),⁽¹³⁹⁾

¹²⁹ P. F. KELLY, J. D. WOOLLINS, *Polyhedron* **12**, 1129–33 (1993).

¹³⁰ P. F. KELLY, A. M. Z. SLAWIN, D. J. WILLIAMS and J. D. WOOLLINS, *Polyhedron* **9**, 1567–71 (1990).

¹³¹ E. G. AWERE, J. PASSMORE, P. S. WHITE and T. M. KLAPÖTKE, *J. Chem. Soc., Chem. Commun.*, 1415–7 (1989).

¹³² R. WOLLERT, B. NEUMÜLLER and K. DEHNICKE, *Z. anorg. allg. Chem.* **616**, 191–4 (1992).

¹³³ M. BRÖSCHAG, T. M. KLAPÖTKE, I. C. TORNIERTH-OETTING and P. S. WHITE, *J. Chem. Soc., Chem. Commun.*, 1390–1 (1992).

¹³⁴ A. HAAS, J. KASPROWSKI, K. ANGERMUND, P. BETZ, C. KRÜGER, Yi-H. TSAY and S. WERNER, *Chem. Ber.* **124**, 1895–906 (1991).

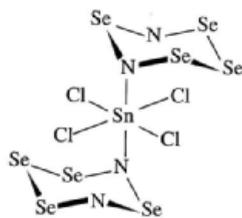
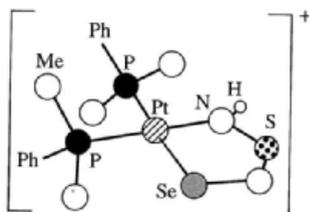
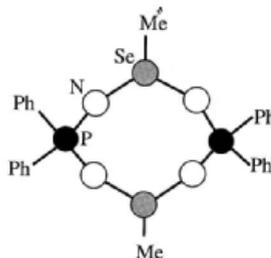
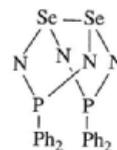
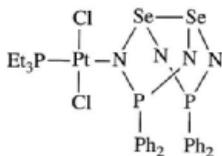
¹³⁵ S. VOGLER, M. SCHÄFER and K. DEHNICKE, *Z. anorg. allg. Chem.* **606**, 73–8 (1991).

¹³⁶ C. A. O'MAHONEY, I. P. PARKIN, D. J. WILLIAMS and J. D. WOOLLINS, *Polyhedron* **8**, 2215–7 (1989).

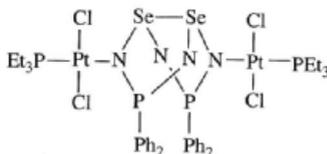
¹³⁷ P. F. KELLY, I. P. PARKIN, A. M. Z. SLAWIN, D. J. WILLIAMS and J. D. WOOLLINS, *Angew. Chem., Int. Edn. Engl.* **28**, 1047–9 (1989).

¹³⁸ T. CHIVERS, D. D. DOXSEE and J. F. FAIT, *J. Chem. Soc., Chem. Commun.*, 1703–5 (1989).

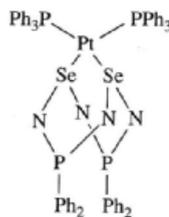
¹³⁹ T. CHIVERS, D. D. DOXSEE, R. W. HILTS, A. MEETSMA, M. PARVEZ and J. C. VAN DE GRAMPPEL, *J. Chem. Soc., Chem. Commun.*, 1330–2 (1992).

(9) $[\text{SnCl}_4(\text{N}_2\text{Se}_4)_2]$ (10) $[\text{Pt}(\text{SeSN}_2\text{H})(\text{PMe}_2\text{Ph}_2)_2]^+$ (11) $[(\text{Ph}_2\text{P})_2\text{N}_4(\text{SeMe})_2]$ (12) $[(\text{Ph}_2\text{P})_2\text{N}_4\text{Se}_2]$ 

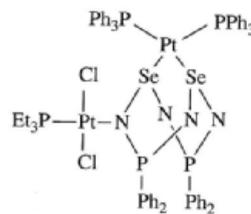
(13)



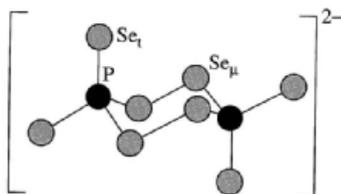
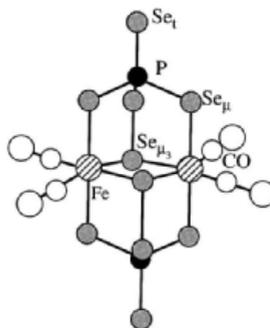
(14)



(15)



(16)

(17) $\text{P}_2\text{Se}_8^{2-}$ (18) $[\text{Fe}_2(\text{CO})_4(\text{PSe}_5)_2]$

Reaction of P_4Se_4 with soluble polyselenides afforded the first isolated P/Se anion, the yellow $\text{P}_2\text{Se}_8^{2-}$ (17) which further reacts with $\text{Fe}(\text{CO})_5$ to generate the novel brown cluster anion $[\text{Fe}_2(\text{CO})_4(\text{PSe}_5)_2]$ (18).⁽¹⁴⁰⁾ Numerous other examples are known; indeed, the whole field is still rapidly developing and many new types of compound are being synthesized and characterized each year.

Tellurium-chalcogen-nitrogen chemistry is also burgeoning. Typical examples include the red crystalline $\text{Te}(\text{NSO})_2$,⁽¹⁴¹⁾ isomorphous with

$\text{Se}(\text{NSO})_2$ (5), and the cationic heterocycle $[\text{FTeNSNSeNSN}]^+[\text{TeF}_5]^-$, which is formed, together with $[\{\text{SeNSNSe}\}_2]^{2+}[\text{TeF}_5]^{2-}$, when $\text{Se}(\text{NSO})_2$ reacts with TeF_4 in CH_2Cl_2 .⁽¹⁴²⁾ The first stable tellurophosphorane complexes $[\text{M}(\text{CO})_5(\text{Te}=\text{PBu}_3^t)]$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) were prepared as dark-red crystals by photolysis of the hexacarbonyls in the presence of $\text{Bu}_3^t\text{P}=\text{Te}$, and the expected bent coordination at Te was confirmed by X-ray analysis (angle $\text{W}-\text{Te}-\text{P}$ 120.1°).⁽¹⁴³⁾ By Contrast, reaction of $\text{Et}_3\text{P}=\text{Te}$ with $[\text{Mn}(\text{CH}_2\text{Ph})(\text{CO})_5]$ in refluxing toluene results in the insertion of Te into

¹⁴⁰ J. ZHAO, W. T. PENNINGTON and J. W. KOLIS, *J. Chem. Soc., Chem. Commun.*, 265–6 (1992).

¹⁴¹ A. HAAS and R. POHL, *Chimia* **43**, 261–2 (1989). See also R. BOESE, F. DWORAK, A. HAAS and M. PRYKA, *Chem. Ber.* **128**, 477–80 (1995).

¹⁴² A. HAAS and M. PRYKA, *Chem. Ber.* **128**, 11–22 (1995).

¹⁴³ N. KUHN, H. SCHUMANN and G. WOLMERSHÄUSER, *J. Chem. Soc., Chem. Commun.*, 1595–7 (1985).

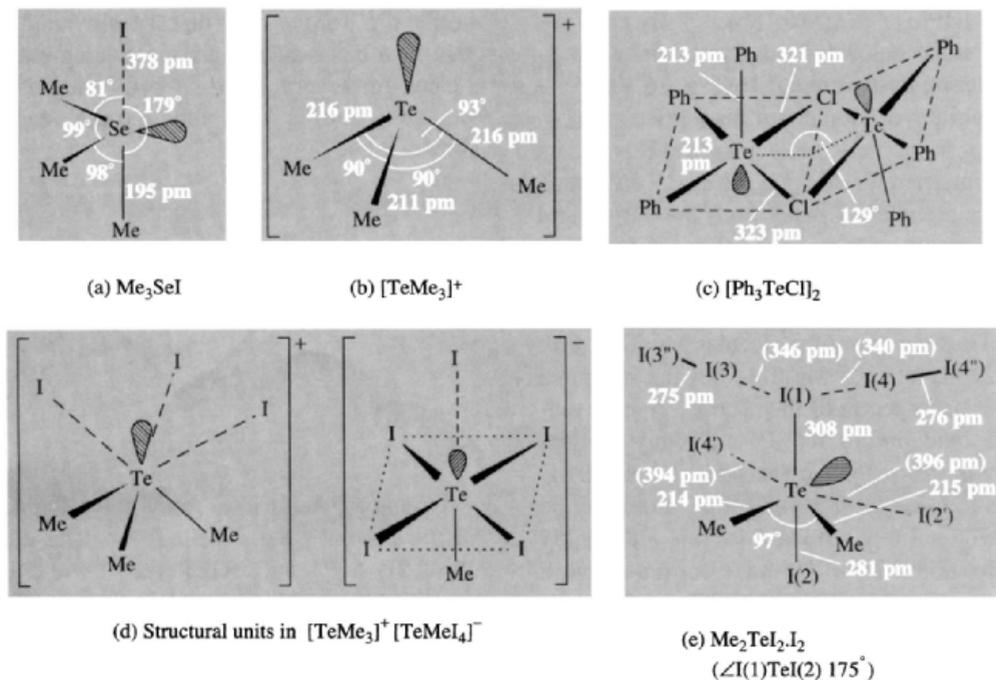


Figure 16.18 Some coordination environments of Se and Te in their organohalides.

the selenides R_2Se and diselenides R_2Se_2 .⁽¹⁾ Detailed discussion of these and related tellurium compounds falls outside the scope of the present treatment. Other compounds such as the cyano derivatives (p. 778) and CSe_2 , COSe , COTe and CSTe (p. 754) have already been briefly mentioned.

Tellurocarbonyl derivatives $\text{R}^1\text{C}(=\text{Te})\text{OR}^2$ and telluroamides, e.g. $\text{PhC}(=\text{Te})\text{NMe}_2$ (mp 73°) have been prepared⁽¹⁵⁰⁾ and shown to be similar to, though more reactive than, the corresponding seleno derivatives.

Reaction of $[\text{Se}_4]^{2+}[\text{AsF}_6]_2^-$ with Ph_2Se_2 in liquid SO_2 gives the bright orange compound $[\text{Se}_6\text{Ph}_2]^{2+}[\text{AsF}_6]_2^- \cdot \text{SO}_2$ in which the Se_6 ring adopts the boat conformation with pendent Ph groups in the 1- and 4-positions.⁽¹⁵¹⁾ By contrast the reaction of K_2CO_3 with red-Se in acetone in

the presence of $[(\text{Ph}_3\text{P})_2\text{N}]\text{Cl}$ yields red crystals of $[(\text{Ph}_3\text{P})_2\text{N}]^+[\text{Se}_5\text{C}(\text{Se})\text{C}(\text{O})\text{Me}]^-$; the anion, which adopts the chair conformation, is the first example of an Se_5C ring, and the C atom has exocyclic $=\text{Se}$ and $-\text{C}(\text{O})\text{Me}$ groups attached.⁽¹⁵²⁾

Stoichiometry is frequently an inadequate guide to structure in organo-derivatives of Se and Te particularly when other elements (such as halogens) are also present. This arises from the incipient tendency of many of the compounds to undergo ionic dissociation or, conversely, to increase the coordination number of the central atom by dimerization or other oligomeric interactions. Thus Me_3SeI features pyramidal ions $[\text{SeMe}_3]^+$ but these are each associated rather closely with 1 iodide which is colinear with 1 $\text{Me}-\text{Se}$ bond to give a distorted pseudotrigonal bipyramidal configuration (Fig. 16.18a).⁽¹²⁵⁾ A regular pyramidal cation can, however, be obtained by use of a large non-coordinating counteranion, as in

¹⁵⁰ K. A. LERSTRUP and L. HENRIKSEN, *J. Chem. Soc., Chem. Commun.*, 1102-3 (1979) and references therein.

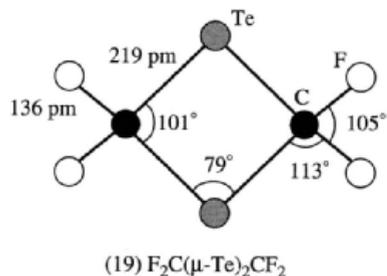
¹⁵¹ R. FAGGIANI R. J. GILLESPIE and J. W. KOLIS *J. Chem. Soc., Chem. Commun.*, 592-3 (1987).

¹⁵² T. CHIVERS, M. PARVEZ, M. PEACH and R. VOLLMERHAUS, *J. Chem. Soc., Chem. Commun.*, 1539-40 (1992).

[TeMe₃]⁺[BPh₄]⁻ (Fig. 16.18b).⁽¹⁵³⁾ By contrast, Ph₃TeCl is a chloride-bridged dimer with 5-coordinate square-pyramidal Te (Fig. 16.13c).⁽¹⁵⁴⁾ The possibility of isomerism also exists: e.g. 4-coordinate, monomeric molecular Me₂TeI₂ and its ionic counterpart [TeMe₃]⁺[TeMeI₄]⁻ in which interionic interactions make both the cation and the anion pseudo-6-coordinate (Fig. 16.18d).⁽¹²⁵⁾ Further complications obtrude when the halogen itself is capable of forming polyhalide units in the crystal. Thus reaction of molecular Me₂TeI₂ with iodine readily affords Me₂TeI₄ but the chemical behaviour and spectra of the product give no evidence for oxidation to Te(VI), and X-ray analysis indicates the formation of an adduct Me₂TeI₂·I₂ in which the axially disposed iodine atoms of the pseudo-trigonal-bipyramidal Me₂TeI₂ are weakly bonded to molecules of iodine to form a network as shown in Fig. 16.18e⁽¹⁵⁵⁾ (cf. TlI₃, p. 239).

Among the range of homoleptic organotellurium compounds that have recently been synthesized are the perfluoroalkyl derivatives Te(C_nF_{2n+1})₄, (n = 1–4).⁽¹⁵⁶⁾ Of these, the yellow oily liquid Te(CF₃)₄ is the least stable, being both light- and temperature-sensitive. It reacts with fluorides to give the complex anion [Te(CF₃)₄F]⁻ and with fluoride-ion acceptors to form the cation [Te(CF₃)₃]⁺. Te(CF₃)₄ is made by reacting Te(CF₃)₂Cl₂ with Cd(CF₃)₂ in MeCN. The higher members can be made directly from TeCl₄ and Cd(CF₃)₂ are also viscous yellow liquids. The related TeMe₄ was first made in 1989 as a yellow pyrophoric liquid by treating TeCl₄ with LiMe in ether at -78°;⁽¹⁵⁷⁾ it can be oxidized by XeF₂ to the volatile white solid Me₄TeF₂ which, when treated with ZnMe₂, gave TeMe₆ as a white

solid.⁽¹⁵⁸⁾ TeMe₆, the first peralkylated derivative of a hexavalent main-group element, can be heated for several hours at 140° without decomposition, and is thus much more stable than TeMe₄.



Organopolytellurides (and polyselenides) are also known, e.g. ArTeTeAr (Ar = 2, 4, 6-Ph₃C₆H₂-)⁽¹⁵⁹⁾ and RTeTeTeR (R = (Me₃Si)₃-C),⁽¹⁶⁰⁾ the stabilizing rôle of the bulky end groups is evident. [The related “isoelectronic” cation Bu₃P⁺TeTeTePBu₃²⁺ can also be noted;⁽¹⁶¹⁾ it is prepared by oxidizing the tellurophosphorane Bu₃P = Te (see p. 785) using ferricenium salts.] Related compounds are R₂Se_x (x = 2–7) and (RSe)₂S_y (y = 1–15).⁽¹⁶²⁾ Other compounds of note are the first “telluroketone”, Te = CF₂,⁽¹⁶³⁾ a thermally unstable violet compound which readily dimerizes even below room temperature to the dark-red crystalline 1,3-ditelluretane (19). Cocondensation with its analogue, Se = CF₂ yields the corresponding volatile orange solid, 1-selena-3-telluretane, F₂C^{Te}TeCF₂Se.

¹⁵⁸ L. AHMED and J. A. MORRISON, *J. Am. Chem. Soc.* **112**, 7411–13 (1990).

¹⁵⁹ E. S. LANG, C. MAICHLE-MÖSSMER and J. STRÄHLE, *Z. anorg. allg. Chem.* **620**, 1678–85 (1994).

¹⁶⁰ F. SLADKY, B. BILDSTEIN, C. RIEKER, A. GIEREN, H. BETZ and T. HÜBNER, *J. Chem. Soc., Chem. Commun.*, 1800–1 (1985).

¹⁶¹ N. KUHN, H. SCHUMANN and R. BOESE, *J. Chem. Soc., Chem. Commun.*, 1257–8 (1987).

¹⁶² M. PRIDÖHL and R. STEUDEL, *Polyhedron* **12**, 2577–85 (1993).

¹⁶³ R. BOESE, A. HAAS and C. LIMBERG, *J. Chem. Soc., Chem. Commun.*, 1378–9 (1991) and *J. Chem. Soc., Dalton Trans.*, 2547–56 (1993).

¹⁵³ R. F. ZIOLO and J. M. TROUP, *Inorg. Chem.* **18**, 2271–4 (1979). See also, however, M. J. COLLINS, J. A. RIPMEESTER and J. F. SAWYER, *J. Am. Chem. Soc.* **110**, 8583–90 (1988).

¹⁵⁴ R. F. ZIOLO and M. EXTINE, *Inorg. Chem.* **19**, 2964–7 (1980).

¹⁵⁵ H. PRITZKOW, *Inorg. Chem.* **18**, 311–13 (1979).

¹⁵⁶ D. NAUMANN, H. BUTLER, J. FISCHER, J. HANKE, J. MOGIAS and B. WILKES, *Z. anorg. allg. Chem.* **608**, 69–72 (1992).

¹⁵⁷ R. W. GEDRIDGE, D. C. HARRIS, K. T. HIGA and R. A. NISSAN, *Organometallics* **8**, 2817–20 (1989).