

Figure 16.10 Structures of some metal-polytelluride complexes.

in $[\text{NEt}_4]_3[\text{Fe}_4(\mu_3\text{-Te})_4(\text{TePh})_4] \cdot 2\text{MeCN}$ ⁽⁶⁸⁾ and, perhaps surprisingly, in NaTe_3 which has cubane-like interlinked clusters of Te_{12}^{6-} .⁽⁶⁹⁾ The trinuclear anion $[\text{Cr}_3\text{Te}_{24}]^{3-}$ has the same structure as its Se analogue (p. 763).⁽⁵¹⁾ Mention could also be made of the planar ion $[\text{TeS}_3]^{2-}$ and the spiro-bicyclic $[\text{Te}(\eta^2\text{-S}_5)_2]^{2-}$ in which the Te atom is also planar⁽⁷⁰⁾ (cf. Se_{11}^{2-} in Fig. 16.8).

⁶⁸ W. SIMON, A. WILK, B. KREBS and G. HENKEL, *Angew. Chem. Int. Edn. Engl.* **26**, 1009–10 (1987).

⁶⁹ P. BÖTTCHER and R. KELLER, *Z. anorg. allg. Chem.* **542**, 144–52 (1986).

⁷⁰ W. BUBENHEIM, G. FRENZEN and U. MÜLLER, *Z. anorg. allg. Chem.* **620** 1046–50 (1994).

16.2 Compounds of selenium, tellurium and polonium

16.2.1 Selenides, tellurides and polonides

All three elements combine readily with most metals and many non-metals to form binary chalcogenides. Indeed, selenides and tellurides are the most common mineral forms of these elements (p. 748). Nonstoichiometry abounds, particularly for compounds with the transition elements (where electronegativity differences are minimal and variable valency is favoured), and many of the chalcogenides can be considered

as metallic alloys. Many such compounds have important technological potentialities for solid-state optical, electrical and thermoelectric devices and have been extensively studied. For the more electropositive elements (e.g. Groups 1 and 2), the chalcogenides can be considered as "salts" of the acids, H_2Se , H_2Te , and H_2Po (see next subsection).

The alkali metal selenides and tellurides can be prepared by direct reaction of the elements at moderate temperatures in the absence of air, or more conveniently in liquid ammonia solution. They are colourless, water soluble, and readily oxidized by air to the element. The structures adopted are not unexpected from general crystallochemical principles. Thus Li_2Se , Na_2Se and K_2Se have the antifluorite structure (p. 118); $MgSe$, $CaSe$, $SrSe$, $BaSe$, $ScSe$, YSe , $LuSe$, etc., have the rock-salt structure (p. 242); $BeSe$, $ZnSe$ and $HgSe$ have the zinc-blende structure (p. 1210); and $CdSe$ has the wurtzite structure (p. 1210). The corresponding tellurides are similar, though there is not a complete 1:1 correspondence. Polonides can also be prepared by direct reaction and are amongst the stablest compounds of this element: Na_2Po has the antifluorite structure; the NaCl structure is adopted by the polonides of Ca, Ba, Hg, Pb and the lanthanide elements; $BePo$ and $CdPo$ have the ZnS structure and $MgPo$ the nickel arsenide structure (p. 556). Decomposition temperatures of these polonides are about $600 \pm 50^\circ C$ except for the less-stable $HgPo$ (decomp 300°) and the extremely stable lanthanide derivatives which do not decompose even at 1000° (e.g. $PrPo$ mp 1253° , $TmPo$ mp $2200^\circ C$).

Transition-element chalcogenides are also best prepared by direct reaction of the elements at 400 – $1000^\circ C$ in the absence of air. They tend to be metallic nonstoichiometric alloys though intermetallic compounds also occur, e.g. $Ti_{\sim 2}Se$, $Ti_{\sim 3}Se$, $TiSe_{0.95}$, $TiSe_{1.05}$, $Ti_{0.9}Se$, Ti_3Se_4 , $Ti_{0.7}Se$, Ti_5Se_8 , $TiSe_2$, $TiSe_3$, etc.^(71,72)

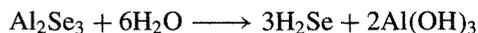
Fuller details of these many compounds are in the references cited.

Most selenides and tellurides are decomposed by water or dilute acid to form H_2Se or H_2Te but the yields, particularly of the latter, are poor.

Polychalcogenides are less stable than polysulfides (p. 681). Reaction of alkali metals with Se in liquid ammonia affords M_2Se_2 , M_2Se_3 and M_2Se_4 , and analogous polytellurides have also been reported (see preceding section). However many of these compounds are rather unstable thermally and tend to be oxidized in air.

16.2.2 Hydrides

H_2Se (like H_2O and H_2S) can be made by direct combination of the elements (above 350°), but H_2Te and H_2Po cannot be made in this way because of their thermal instability. H_2Se is a colourless, offensive-smelling poisonous gas which can be made by hydrolysis of Al_2Se_3 , the action of dilute mineral acids on $FeSe$ or the surface-catalysed reaction of gaseous Se and H_2 :



In this last reaction, conversion at first rises with increase in temperature and then falls because of increasing thermolysis of the product: conversion exceeds $\sim 40\%$ between 350 – 650° and is optimum (64%) at 520° .

H_2Te is also a colourless, foul-smelling toxic gas which is best made by electrolysis of 15 – 50% aqueous H_2SO_4 at a Te cathode at -20° , 4.5 A and 75 – 110 V. It can also be made by hydrolysis of Al_2Te_3 , the action of hydrochloric acid on the tellurides of Mg, Zn or Al, or by reduction of Na_2TeO_3 with $TiCl_3$ in a buffered solution. The compound is unstable above 0° and decomposes in moist air and on exposure to light. H_2Po is even less stable and has only been made in trace amounts ($\sim 10^{-10}$ g scale) by reduction of Po using Mg foil/dilute HCl and the reaction followed by radioactive tracer techniques.

⁷¹ D. M. CHIZHIKOV and V. P. SHCHASTLIVYI, *Selenium and Selenides*, Collet's, London, 1968, 403 pp.

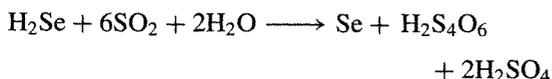
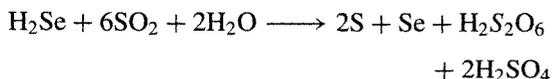
⁷² F. HULLIGER, *Struct. Bonding (Berlin)*, **4**, 83–229 (1968).

Table 16.4 Some physical properties of H₂O, H₂S, H₂Se, H₂Te and H₂Po

Property	H ₂ O	H ₂ S	H ₂ Se	H ₂ Te	H ₂ Po
MP/°C	0.0	-85.6	-65.7	-51	-36(?)
BP/°C	100.0	-60.3	-41.3	-4	+37(?)
$\Delta H_f^\circ/\text{kJ mol}^{-1}$	-285.9	+20.1	+73.0	+99.6	—
Bond length (M-H)/pm	95.7	133.6	146	169	—
Bond angle (H-M-H) (g)	104.5°	92.1°	91°	90°	—
Dissociation constant:					
HM ⁻ , K_1	1.8×10^{-16}	1.3×10^{-7}	1.3×10^{-4}	2.3×10^{-3}	—
M ²⁻ , K_2	—	7.1×10^{-15}	$\sim 10^{-11}$	1.6×10^{-11}	—

Physical properties of the three gases are compared with those of H₂O and H₂S in Table 16.4. The trends are obvious, as is the "anomalous" position of water (p. 623). The densities of liquid and solid H₂Se are 2.12 and 2.45 g cm⁻³. H₂Te condenses to a colourless liquid (d 4.4 g cm⁻³) and then to lemon-yellow crystals. Both gases are soluble in water to about the same extent as H₂S, yielding increasingly acidic solutions (cf. acetic acid $K_1 \sim 2 \times 10^{-5}$). Such solutions precipitate the selenides and tellurides of many metals from aqueous solutions of their salts but, since both H₂Se and H₂Te are readily oxidized (e.g. by air), elementary Se and Te are often formed simultaneously.

H₂Se and H₂Te burn in air with a blue flame to give the dioxide (p. 779). Halogens and other oxidizing agents (e.g. HNO₃, KMnO₄) also rapidly react with aqueous solutions to precipitate the elements. Reaction of H₂Se with aqueous SO₂ is complex, the products formed depending critically on conditions (cf. Wackenroder's solution, p. 716): addition of the selenide to aqueous SO₂ yields a 2:1 mixture of S and Se together with oxoacids of sulfur, whereas addition of SO₂ to aqueous H₂Se yields mainly Se:



H₂Te undergoes oxidative addition to certain organometallic compounds, e.g. [Re(η^5 -C₅Me₅)-

(CO)₂(thf)] reacts in thf solution at 25°C to give [HRe(η^5 -C₅Me₅)(CO)₂(TeH)] and related dinuclear complexes.⁽⁷³⁾ The Te analogue of the hydroxide ion, TeH⁻, has been reported from time to time but has only recently been properly characterized crystallographically, in [PPh₄]⁺[TeH]⁻⁽⁷⁴⁾

16.2.3 Halides

As with sulfur, there is a definite pattern to the stoichiometries of the known halides of the heavier chalcogens. Selenium forms no binary iodides whereas the more electropositive Te and Po do. Numerous chlorides and bromides are known for all 3 elements, particularly in oxidation states +1, +2 and +4. In the highest oxidation state, +6, only the fluorides MF₆ are known for the 3 elements; in addition SeF₄ and TeF₄ have been characterized but no fluorides of lower oxidation states except the fugitive FSeSeF, Se=SeF₂ and SeF₂ which can be trapped out at low temperature.^(75,76) The compound previously thought to be Te₂F₁₀ is now known to be O(TeF₅)₂^(76,77) (p. 778). Finally, Te forms a range of curious lower halides which

⁷³ W. A. HERRMANN, C. HECHT, E. HERDTWECK and H.-J. KNEUPER, *Angew. Chem. Int. Edn. Engl.* **26**, 132-4 (1987).

⁷⁴ J. C. HUFFMAN and R. C. HAUSHALTER, *Polyhedron* **8**, 531-2 (1989).

⁷⁵ B. COHEN and R. D. PEACOCK, *Adv. Fluorine Chem.* **6**, 343-85 (1970).

⁷⁶ E. ENGELBRECHT and F. SLADKY, *Adv. Inorg. Chem. Radiochem.* **24**, 189-223 (1981). This review also includes oxofluorides of Se and Te, and related anions.

⁷⁷ P. M. WATKINS, *J. Chem. Educ.*, **51**, 520-1 (1974).

are structurally related to the Te_x chains in elementary tellurium.

The known compounds are summarized in Table 16.5 which also lists their colour, mp, bp and decomposition temperature where these have been reported. It will be convenient to discuss the preparation, structure and chemical properties of these various compounds approximately in

ascending order of formal oxidation state. For comparable information on the halides of S, see pp. 683–93.

Lower halides

The phase relations in the tellurium-halogen systems have only recently been elucidated

Table 16.5 Halides of selenium, tellurium and polonium

Oxidation state	Fluorides	Chlorides	Bromides	Iodides
< 1		Te_2Cl Te_3Cl_2 silver grey mp 238° (peritectic)	Te_2Br grey needles mp 224 (peritectic)	Te_2I silver grey [Te_2] ₂ (I ₂) _x ($X \leq i$) metallic black
+1	(FSeSeF) and (Se=SeF ₂) trapped at low temperature	Se_2Cl_2 yellow-brown liquid mp -85°, bp 130° (d)	(β -) Se_2Br_2 blood-red liquid bp 225° (d) (α -SeBr, mp +5°)	α - Te_4I_4 black mp 185°(peritectic) β -TeI black
+2	(SeF ₂) trapped at low temperature	(SeCl ₂) d in vapour ("TeCl ₂ ") black eutectic PoCl ₂ dark ruby red mp 355°, subl 130°	(SeBr ₂) d in vapour ("TeBr ₂ ") brown d (see text) PoBr ₂ purple-brown mp 270° (d)	(PoI ₂) impure (from decomp of PoI ₄ at 200°)
+4	SeF ₄ colourless liquid mp -10°, bp 101° TeF ₄ colourless mp 129° d > 194° PoF ₄ (?) solid from decomp of PoF ₆	Se ₄ Cl ₁₆ colourless mp 305°, subl 196° Te ₄ Cl ₁₆ pale-yellow solid. maroon liquid mp 223°, bp 390° PoCl ₄ yellow d > 200° to PoCl ₂ mp 300°, bp ~ 390° extrapolated	α -Se ₄ Br ₁₆ orange-red mp 123° (also β -Se ₄ Br ₁₆) Te ₄ Br ₁₆ yellow mp 388° (under Br ₂) bp 414° (under Br ₂) PoBr ₄ bright red mp 330°, bp 360°/200 mmHg	Te ₄ I ₁₆ black mp 280°, d 100° PoI ₄ black d > 200°
+6	SeF ₆ colourless gas mp -35° (2 atm), subl -47° TeF ₆ colourless gas mp -38°, subl -39°		<i>Mixed halides</i> TeBr ₂ Cl ₂ yellow solid, ruby-red liquid mp 292°, bp 415° TeBr ₂ I ₂ garnet-red crystals mp 325°, d 420° PoBr ₂ Cl ₂ salmon pink (PoCl ₂ + Br ₂ vap)	

and the results show a series of subhalides with various structural motifs based on the helical-chain structure of Te itself.⁽⁷⁸⁾ These are summarized in Fig. 16.11. Thus, reaction of Te and Cl₂ under carefully controlled conditions in a sealed tube⁽⁷⁹⁾ results in Te₃Cl₂ (Fig. 16.11b) in which every third Te atom in the chain is oxidized by addition of 2 Cl atoms, thereby forming a series of 4-coordinate pseudo-trigonal-bipyramidal groups with axial Cl atoms linked by pairs of unmodified Te atoms –Te–Te–TeCl₂–Te–Te–TeCl₂–.⁽⁸⁰⁾ Te₂Br and Te₂I consist of zigzag chains of Te in planar arrangement (Fig. 16.11c); along the chain is an alternation of trigonal pyramidal (pseudo-tetrahedral) and square-planar (pseudo-octahedral) Te atoms. These chains are joined in pairs by cross-linking at the trigonal pyramidal Te atoms, thereby forming a ribbon of fused 6-membered Te rings in the boat configuration.⁽⁸⁰⁾ A similar motif occurs in β-TeI (Fig. 16.11d) which is formed by rapidly cooling partially melted α-TeI (see below) from 190°: in this case the third bond from the trigonal pyramidal Te atoms carries an I atom instead of being cross-linked to a similar chain.⁽⁸¹⁾ The second, more stable modification, α-TeI, features tetrameric molecules Te₄I₄ which are themselves very loosely associated into chains by Te–I...Te links (Fig. 16.11e); the non-planar Te₄ ring comprises two non-adjacent 3-coordinate trigonal pyramidal Te atoms bridged on one side by a single 2-coordinate Te atom and on the other by a 4-coordinate planar >TeI₂ group. An unrelated structure motif is found in the

unusual intercalation compound, [(Te₂)₂(I₂)_x] (x = 0.42–1.0),⁽⁸²⁾ which is obtained as shiny, metallic-black air-stable crystals by hydrothermal reaction of 67% HI (aq.) on a 1:1 mixture of Te and GeTe at ca. 170° followed by slow cooling (18 h). The structure comprises planar double layers of Te₂ units intercalated by I₂ up to the limiting formula [(Te₂)₂I₂]. The Te atoms within the double layers exhibit distorted tetragonal pyramidal coordination with one short and four longer Te–Te distances (271.3 and 332.3 pm, respectively; cf. distances in Fig. 16.11). The I–I distance within the I₂ molecules is 286.6 pm (cf. 271.5 pm in solid iodine, p. 803). The semiconductivity and nonlinear optical properties of these various tellurium subhalides have been much studied for possible electronic applications.

The only other “monohalides” of these chalcogens are the highly coloured heavy liquids Se₂Cl₂ (d₂₅ 2.774 g cm⁻³) and Se₂Br₂ (d₁₅ 3.604 g cm⁻³). Both can be made by reaction of the stoichiometric amounts of the elements or better, by adding the halogen to a suspension of powdered Se in CS₂. Reduction of SeX₄ with 3Se in a sealed tube at 120° is also effective. Se₂Br₂ has a structure similar to that of S₂Cl₂ and S₂F₂ (pp. 689, 684) with a dihedral angle of 94°, angle Br–Se–Se 104° and a rather short Se–Se bond (224 pm, cf. 233.5 pm in monoclinic Se₈ and 237.3 pm in hexagonal Se_∞).⁽⁸³⁾ The structure of Se₂Cl₂ has not been determined but is probably similar. Se₂Br₂ is, in fact, the metastable molecular form (also known as β-SeBr); the structure of the more stable α-SeBr is as yet unknown.

Several mixed species have been identified in nonaqueous solutions by ⁷⁷Se nmr spectroscopy. These include BrSeSeCl, Se₃X₂ and Se₄X₂,⁽⁸⁴⁾ and ClSeSeCl, BrSeSeCl, ClSeSBr and

⁷⁸ R. KNIEP and A. RABENAU, *Topics in Current Chemistry* **111**, 145–92 (1983).

⁷⁹ A. RABENAU and H. RAU, *Z. anorg. allg. Chem.* **395**, 273–9 (1973).

⁸⁰ R. KNIEP, D. MOOTZ and A. RABENAU, *Angew. Chem. Int. Edn. Engl.* **12**, 499–500 (1973). M. TAKEDA and N. N. GREENWOOD, *J. Chem. Soc., Dalton Trans.*, 631–6 (1976).

⁸¹ R. KNIEP, D. MOOTZ and A. RABENAU, *Angew. Chem. Int. Edn. Engl.* **13**, 403–4 (1973). More complex chain and ribbon structures are observed for the ternary compounds α-AsSeI, β-AsSeI, α-AsTeI and β-AsTeI, all of which are isolectronic with Se_∞ and Te_∞ (R. KNIEP and H. D. RESKI, *Angew. Chem. Int. Edn. Engl.* **20**, 212–4 (1981)).

⁸² R. KNIEP and H.-J. BEISTER, *Angew. Chem. Int. Edn. Engl.* **24**, 393–4 (1985).

⁸³ D. KATRYNIOK and R. KNIEP, *Angew. Chem. Int. Edn. Engl.* **19**, 645 (1980).

⁸⁴ M. LAMOUREUX and J. MILNE, *Polyhedron* **9**, 589–95 (1990).

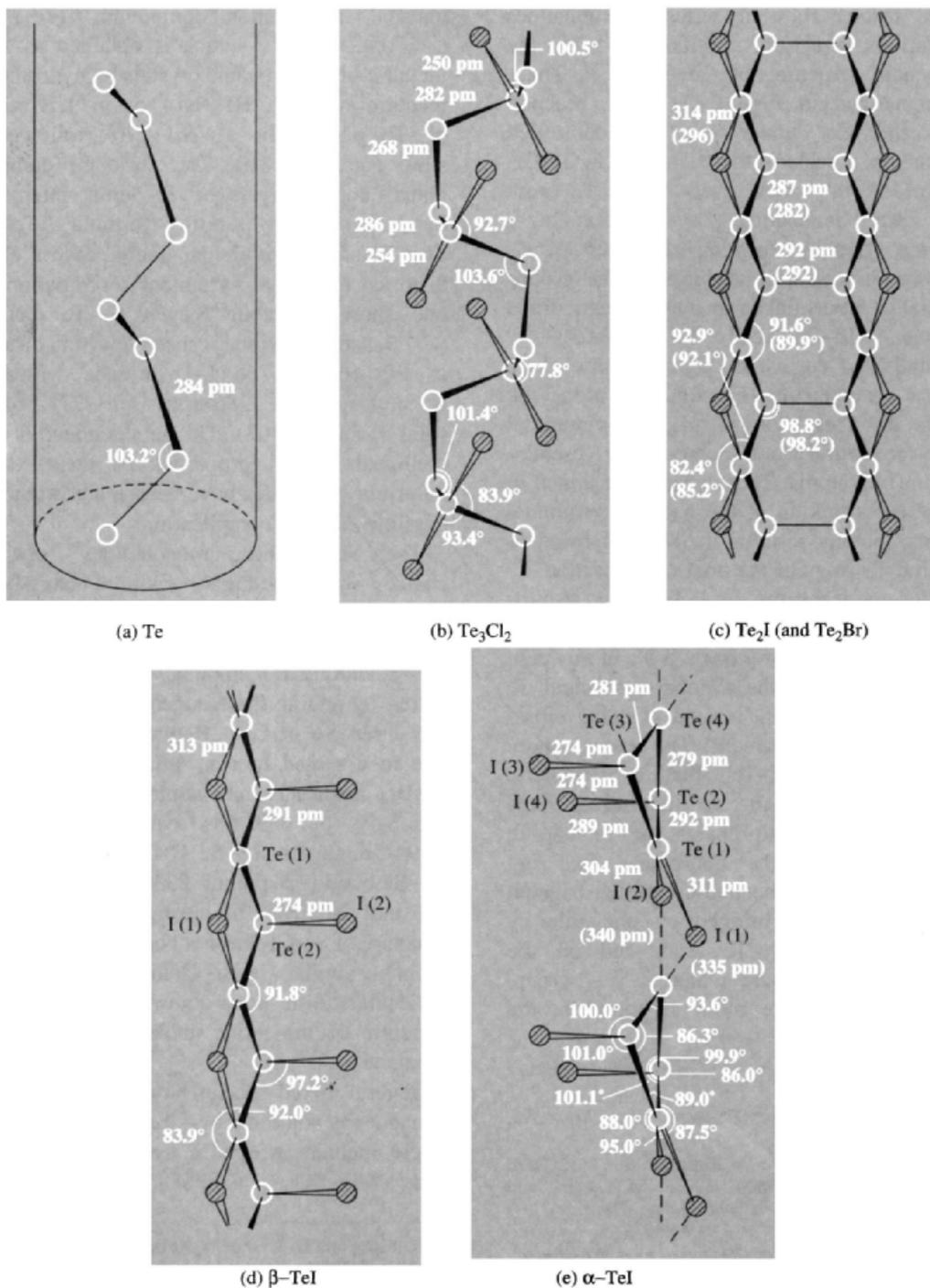


Figure 16.11 Structural relations between tellurium and its subhalides: (a) tellurium, (b) Te_3Cl_2 , (c) Te_2Br and Te_2I , (d) $\beta\text{-TeI}$, and (e) $\alpha\text{-TeI}$.

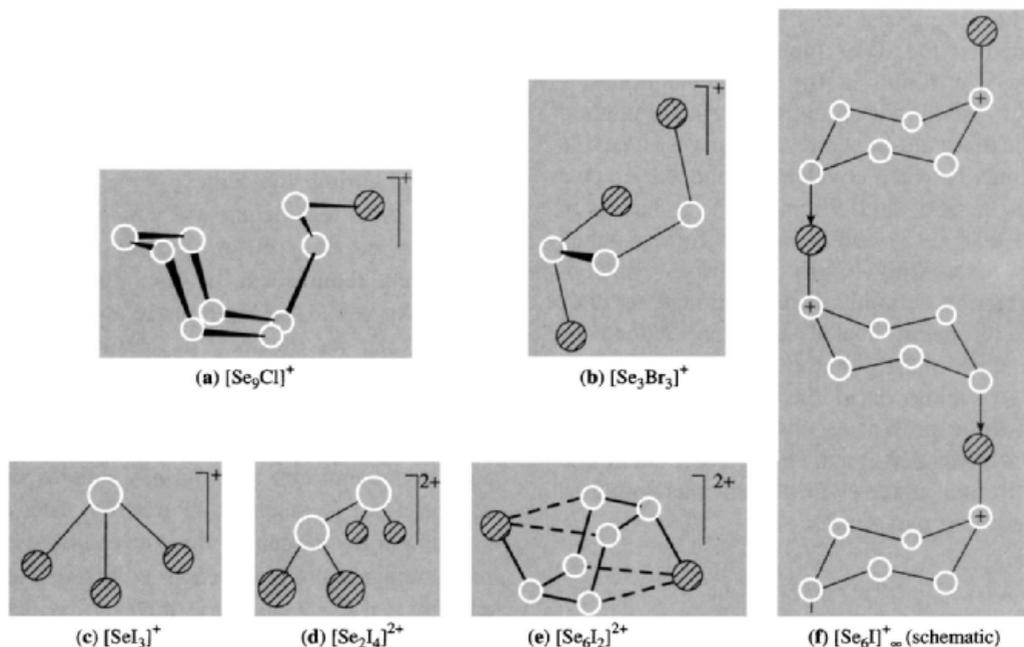


Figure 16.12 Structures of some selenium subhalide cations.

BrSeSBr .⁽⁸⁵⁾ ClSeSCl , formed by mixing solutions of S_2Cl_2 and Se_2Cl_2 , has been reacted with titanocene pentasulfide (p. 672) to give mainly S_7 , SeS_6 and $1,2\text{-Se}_2\text{S}_5$, plus smaller amounts of 6-, 8-, 9- and 12-membered Se/S ring molecules.⁽⁸⁶⁾ The related reaction with SeBr_2 ($\text{SeBr}_4 + \text{Se}$) in MeCN yields similar Se/S heterocycles.⁽⁸⁷⁾

It is also convenient to mention here several cationic subhalide species that have recently been synthesized. Reaction of Se with $[\text{NO}][\text{SbCl}_6]$ in liquid SO_2 yields lustrous dark red crystals of $[\text{Se}_9\text{Cl}]^+[\text{SbCl}_6]^-$ which is the first example of a 7-membered Se ring, $[\text{cyclo-}\text{Se}_7\text{-SeSeCl}]^+$ (Fig. 16.12a).⁽⁸⁸⁾ Again, reaction of stoichiometric amounts of Se (or S), Br_2

and AsF_5 in liquid SO_2 yields dark red crystals or $[\text{Br}_2\text{Se-SeSeBr}]^+[\text{AsF}_6]^-$ (Fig. 16.12b)⁽⁸⁹⁾ or its S analogue. The first known binary Se/I species (albeit cationic rather than neutral) have been prepared⁽⁹⁰⁾ by reaction of Se_4^{2+} and I_2 in SO_2 : The species SeI_3^+ , $\text{Se}_2\text{I}_4^{2+}$, $\text{Se}_6\text{I}_2^{2+}$ were identified by ^{77}Se nmr spectroscopy and subsequently assigned the definitive structures shown in Fig. 16.12c,d,e after X-ray diffraction analysis.⁽⁹¹⁾ The polymeric cation $[\text{Se}_6\text{I}]_\infty^+$ is also shown, (f).

Paradoxically, the most firmly established dihalides of the heavier chalcogens are the dark ruby-red PoCl_2 and the purple-brown PoBr_2 (Table 16.5). Both are formed by direct reaction of the elements or more conveniently by reducing PoCl_4 with SO_2 and PoBr_4 with H_2S at 25° .

⁸⁵ J. MILNE, *J. Chem. Soc., Chem. Commun.*, 1048–9 (1991).

⁸⁶ R. STEUDEL, B. PLINKE, D. JENSEN and F. BAUMGART, *Polyhedron*, **10**, 1037–48 (1991).

⁸⁷ R. STEUDEL, D. JENSEN and F. BAUMGART, *Polyhedron* **9**, 1199–208 (1990).

⁸⁸ R. FAGGIANI, R. J. GILLESPIE, J. W. KOLIS and K. C. MALHOTRA, *J. Chem. Soc., Chem. Commun.*, 591–2 (1987).

⁸⁹ J. PASSMORE, M. TAJIK and P. S. WHITE, *J. Chem. Soc., Chem. Commun.*, 175–7 (1988).

⁹⁰ M. M. CARNELL, F. GREIN, M. MURCHIE, J. PASSMORE and C.-M. WONG, *J. Chem. Soc., Chem. Commun.*, 225–7 (1986).

⁹¹ T. KLAPÖTKE and J. PASSMORE *Acc Chem. Res.* **22**, 234–40 (1989).

Doubt has been cast on "TeCl₂" and "TeBr₂" mentioned in the older literature since no sign of these was found in the phase diagrams.⁽⁷⁹⁾ However, this is not an entirely reliable method of establishing the existence of relatively unstable compounds between covalently bonded elements (cf. P/S, p. 506, and S/I, p. 691). It has been claimed that TeCl₂ and TeBr₂ are formed when fused Te reacts with CCl₂F₂ or CBrF₃,⁽⁹²⁾ though these materials certainly disproportionate to TeX₄ and Te on being heated and may indeed be eutectic-type phases in the system. SeCl₂ and SeBr₂ are unknown in the solid state but are thought to be present as unstable species in the vapour above SeX₄ and have been identified in equilibrium mixtures in nonaqueous solutions (see preceding paragraph).

Tetrahalides

All 12 tetrahalides of Se, Te and Po are known except, perhaps, for SeI₄. As with PX₅ (p. 498) and SX₄ (p. 691) these span the "covalent-ionic" border and numerous structural types are known; the stereochemical influence of the lone-pair of electrons (p. 377) is also prominent. SeF₄ is a colourless reactive liquid which fumes in air and crystallizes to a white hygroscopic solid (Table 16.5). It can be made by the controlled fluorination of Se (using F₂ at 0°, or AgF) or by reaction of SF₄ with SeO₂ above 100°. SeF₄ can be handled in scrupulously dried borosilicate glassware and is a useful fluorinating agent. Its structure in the gas phase, like that of SF₄ (p. 684), is pseudo-trigonal-bipyramidal with C_{2v} symmetry; the dimensions shown in Fig. 16.13a were obtained by microwave spectroscopy. The same structure persists in solution but, with increasing concentration there is an increasing tendency to association *via* intermolecular F-bridges. The structure in the crystalline phase also has Se bonded to 4F atoms in a distorted pseudo-trigonal bipyramidal configuration as shown in

Fig. 16.13b (Se–F_{ax} 180 pm, Se–F_{eq} 167 pm, with axial and equatorial angles subtended at Se of 169.3° and 96.9°, respectively).⁽⁹³⁾ However, these pseudo-tbp molecules are arranged in layers by weaker intermolecular interactions to neighbouring molecules so as to form an overall distorted octahedral environment with two further Se···F at 266 pm (Fig. 16.13b) somewhat reminiscent of the structure found earlier for TeF₄ (see Fig. 16.13c and below).

TeF₄ can be obtained as colourless, hygroscopic, sublimable crystals by controlled fluorination of Te or TeX₂ with F₂/N₂ at 0°, or more conveniently by reaction of SeF₄ with TeO₂ at 80°. It decomposes above 190° with formation of TeF₆ and is much more reactive than SeF₄. For example, it readily fluorinates SiO₂ above room temperature and reacts with Cu, Ag, Au and Ni at 185° to give the metal tellurides and fluorides. Adducts with BF₃, AsF₅ and SbF₅ are known (see also p. 776). Although probably monomeric in the gas phase, crystalline TeF₄ comprises chains of *cis*-linked square-pyramidal TeF₅ groups (Fig. 16.13c) similar to those in the isoelectronic (SbF₄[–])_n ions (p. 565). The lone-pair is alternately above and below the mean basal plane and each Te atom is displaced some 30 pm in the same direction. However, the local Te environment is somewhat less symmetrical than implied by this idealized description, and the Te–F distances span the range 183–228 pm.⁽⁹³⁾

The other tetrahalides can all readily be made by direct reactions of the elements. Crystalline SeCl₄, TeCl₄ and β-SeBr₄ are isotypic and the structural unit is a cubane-like tetramer of the same general type as [Me₃Pt(μ₃-Cl)]₄ (p. 1168). This is illustrated schematically for TeCl₄ in Fig. 16.13d: each Te is displaced outwards along a threefold axis and thus has a distorted octahedral environment. This can be visualized as resulting from repulsions due to the Te lone-pairs directed towards the cube centre and, in the limit, would result in the separation into

⁹² E. E. AYNSLEY, *J. Chem. Soc.* 3016–9 (1953).
E. E. AYNSLEY and R. H. WATSON, *J. Chem. Soc.* 2603–6 (1955).

⁹³ R. KNIEP, L. KORTE, R. KRYSCHI and W. POLL, *Angew. Chem. Int. Edn. Engl.* 23, 388–9 (1984).

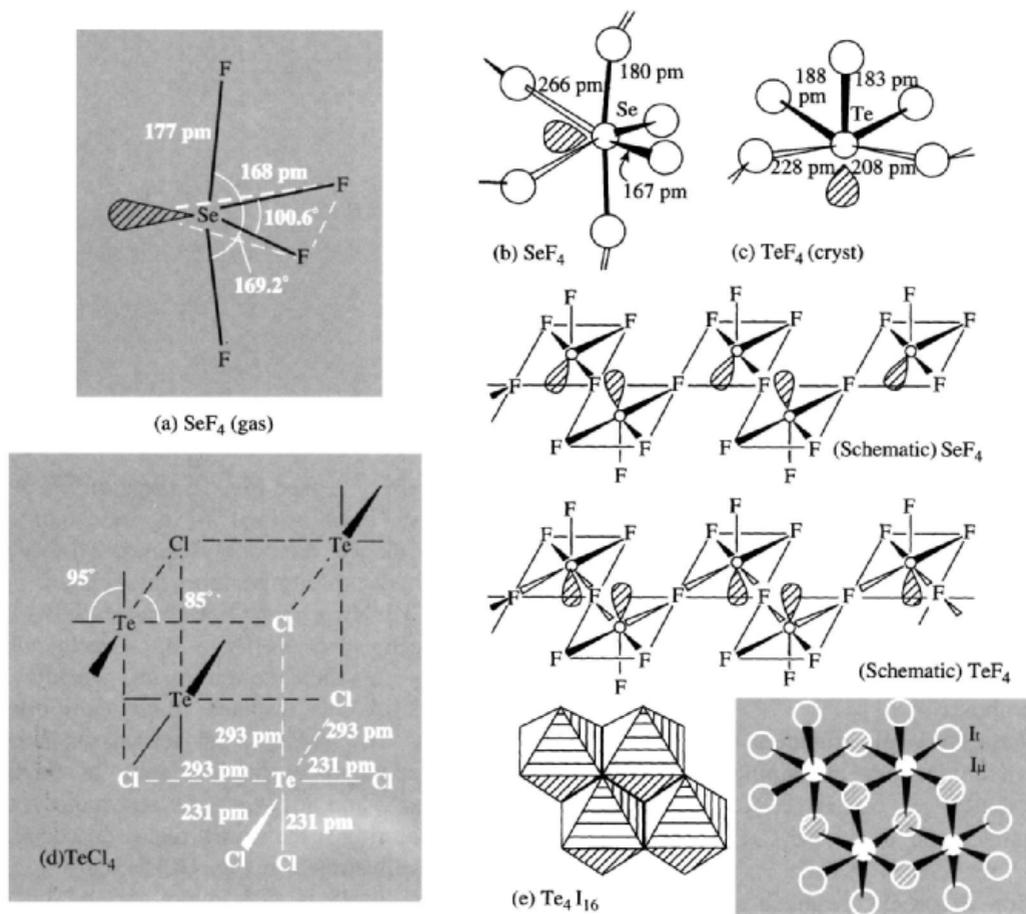
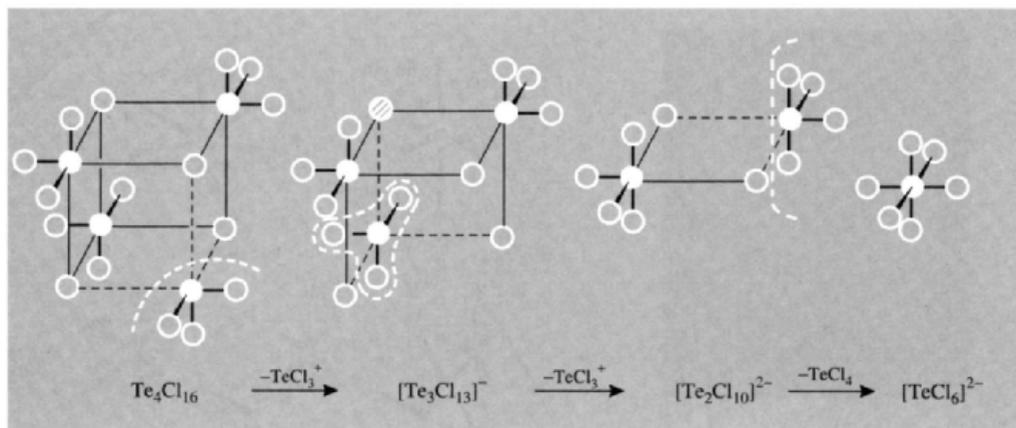


Figure 16.13 Structures of some tetrahalides of Se and Te: (a) SeF_4 (gas), (b) crystalline SeF_4 , and schematic representation of the association of the pseudo-*tpb* molecules (see text), (c) coordination environment of Te in crystalline TeF_4 and schematic representation of the polymerized square pyramidal units, (d) the tetrameric unit in crystalline $(\text{TeCl}_4)_4$, and (e) two representations of the tetrameric molecules in Te_4I_{16} showing the shared edges of the $\{\text{Te}_6\}$ octahedral subunits.

TeCl_3^+ and Cl^- ions. Accordingly, the 3 tetrahalides are good electrical conductors in the fused state, and salts of SeX_3^+ and TeCl_3^+ can be isolated in the presence of strong halide ion acceptors, e.g. $[\text{SeCl}_3]^+[\text{GaCl}_4]^-$, $[\text{SeBr}_3]^+[\text{AlBr}_4]^-$, $[\text{TeCl}_3]^+[\text{AlCl}_4]^-$. In solution, however, the structure depends on the donor properties of the solvent:⁽⁹⁴⁾ in donor solvents such as MeCN, Me_2CO and EtOH the electrical conductivity

and vibrational spectra indicate the structure $[\text{L}_2\text{TeCl}_3]^+\text{Cl}^-$, where L is a molecule of solvent, whereas in benzene and toluene the compound dissolves as a non-conducting molecular oligomer which is tetrameric at a concentration of 0.1 molar but which is in equilibrium with smaller oligomeric units at lower concentrations. Removal of one TeCl_3^+ unit from the cubane-like structure of $\text{Te}_4\text{Cl}_{16}$ leaves the trinuclear anion $\text{Te}_3\text{Cl}_{13}^-$ which can be isolated from benzene solutions as the salt of the large counter-cation Ph_3C^+ ; the anion has the expected C_{3v} structure

⁹⁴ N. N. GREENWOOD, B. P. STRAUGHAN and A. E. WILSON, *J. Chem. Soc. (A)* 2209–12 (1968).



comprising three edge-shared octahedra with a central triply bridging Cl atom.⁽⁹⁵⁾ Removal of a further TeCl_3^+ unit yields the edge-shared bi-octahedral dianion $\text{Te}_2\text{Cl}_{10}^{2-}$ which was isolated as the crystalline salt $[\text{AsPh}_4]_2^+ [\text{Te}_2\text{Cl}_{10}]^{2-}$. Notional removal of a final $\{\text{TeCl}_4\}$ unit leaves the octahedral anion TeCl_6^{2-} (p. 776) as in the scheme above.

Numerous crystal structures have been published of compounds containing the pyramidal cations $\text{Se}^{\text{IV}}\text{Cl}_3^+$, $\text{Se}^{\text{IV}}\text{Br}_3^+$, $\text{Te}^{\text{IV}}\text{Cl}_3^+$, etc.⁽⁹⁶⁾ and the anions $\text{Se}^{\text{II}}\text{Cl}_4^{2-}$, $\text{Se}^{\text{II}}\text{Cl}_6^{2-}$,⁽⁹⁷⁾ $\text{Se}_3\text{Cl}_{13}^-$, $\text{Se}_3\text{Br}_{13}^-$,⁽⁹⁸⁾ SeCl_5^- , TeCl_5^- , TeCl_6^{2-} , etc.⁽⁹⁹⁾ The anion structures are much as expected with the Se^{II} species featuring square planar (pseudo-octahedral) units, and the trinuclear Se^{IV} anions as in the tellurium analogue above. See also p. 776. There are, in addition, a fascinating series of bromoselenate(II) dianions based on fused planar $\{\text{SeBr}_4\}$ units, e.g. $\text{Se}_3\text{Br}_8^{2-}$, $\text{Se}_4\text{Br}_{14}^{2-}$,

and $\text{Se}_5\text{Br}_{12}^{2-}$, (see Fig. 16.14a,b,c)⁽¹⁰⁰⁾. Access has also been gained to a series of novel mixed-valence bromopolyselenate (II,IV) dianions by exploiting the dissociation equilibria $\frac{1}{4}\text{Se}_4\text{Br}_{16} \rightleftharpoons \text{SeBr}_4 \rightleftharpoons \text{SeBr}_2 + \text{Br}_2$ and $2\text{SeBr}_2 \rightleftharpoons \text{Se}_2\text{Br}_2 + \text{Br}_2$. Careful addition of Br_2 to such solutions in weakly polar organic solvents displaces these equilibria and permits the isolation of tetraalkylammonium or tetraphenylphosphonium salts of $\text{Se}_2\text{Br}_8^{2-}$, $\text{Se}_3\text{Br}_{10}^{2-}$, and $\text{Se}_4\text{Br}_{12}^{2-}$, as dark red crystalline salts featuring fused square planar and octahedral units as illustrated in Fig. 16.15a,b,c.⁽¹⁰¹⁾

SeBr_4 itself is dimorphic: the α -form, like β - SeBr_4 mentioned on p. 772, has a cubane-like tetrameric unit ($\text{Se}-\text{Br}_\mu$ 237 pm, $\text{Se}-\text{Br}_\mu$ 297 pm) but the two forms differ in the spacial arrangement of the tetramers.⁽¹⁰²⁾ TeI_4 has yet another structure which involves a tetrameric arrangement of edge-shared $\{\text{TeI}_6\}$ octahedra not previously encountered in binary inorganic compounds (Fig. 16.13e).⁽¹⁰³⁾ The molecule is close to idealized C_{2h} symmetry with each terminal octahedron sharing 2 edges with the 2 neighbouring central octahedra

⁹⁵ B. KREBS and V. PAULAT, *Z. Naturforsch.* **34b**, 900–5 (1979), and references therein.

⁹⁶ B. H. CHRISTIAN, M. J. COLLINS, R. J. GILLESPIE and J. F. SAWYER, *Inorg. Chem.* **25**, 777–88 (1986). B. NEUMÜLLER, C. LAU and K. DEHNICKE, *Z. anorg. allg. Chem.* **622**, 1847–53 (1996).

⁹⁷ B. KREBS, E. LÜHRS, R. WILLMER and F.-P. AHLERS, *Z. anorg. allg. Chem.* **592**, 17–34 (1991). See also H. FOLKERTS, K. DEHNICKE, J. MAGULL, H. GOESMANN and D. FENSKE, *Z. anorg. allg. Chem.* **620**, 1301–6 (1994).

⁹⁸ F.-P. AHLERS, E. LÜHRS and B. KREBS, *Z. anorg. allg. Chem.* **594**, 7–22 (1991).

⁹⁹ B. BORGEN, F. WELLER and K. DEHNICKE, *Z. anorg. allg. Chem.* **596**, 55–61 (1991), and 2nd part of ref. 96.

¹⁰⁰ B. KREBS, F.-P. AHLERS and E. LÜHRS, *Z. anorg. allg. Chem.* **597**, 115–32 (1991).

¹⁰¹ B. KREBS, E. LÜHRS and F.-P. AHLERS, *Angew. Chem. Int. Edn. Engl.* **28**, 187–9 (1989).

¹⁰² P. BORN, R. KNIEP and D. MOOTZ, *Z. anorg. allg. Chem.* **451**, 12–24 (1979).

¹⁰³ V. PAULAT and B. KREBS, *Angew. Chem. Int. Edn. Engl.* **15**, 39–40 (1976).

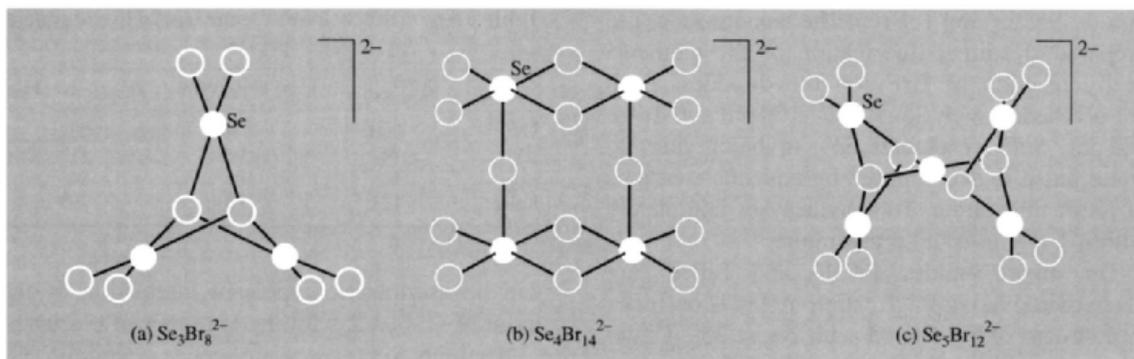


Figure 16.14 Structures of some bromoselenate(II) anions.

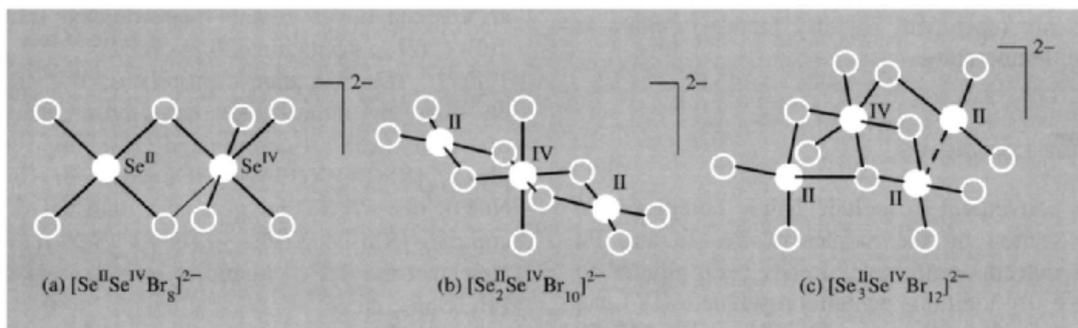
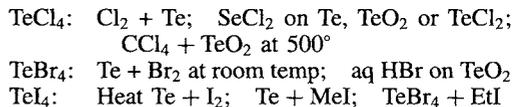


Figure 16.15 Structures of some mixed-valence bromopolyselenate(II,IV) anions.

and each central octahedron sharing 3 edges with its 3 neighbours (Te–I_r 277 pm, Te–I_{μ₂} 311 pm, Te–I_{μ₃} 323 pm). There is no significant intermolecular I··I bonding. Comparison of the structures and bond data for the homologous series TeF₄, TeCl₄(TeBr₄), TeI₄ reveals an increasing delocalization of the Te^{IV} lone-pair. This effect is also observed in the compounds of other *ns*² elements (e.g. Sn^{II}, Pb^{II}, As^{III}, Sb^{III}, Bi^{III}, I^V; see pp. 380, 383, 568) and correlates with the gradation of electronegativities and the polarizing power of the halogens.

The detailed structures of PoX₄ are unknown. Some properties are in Table 16.5. PoF₄ is not well characterized. PoCl₄ forms bright-yellow monoclinic crystals which can be melted under an atmosphere of chlorine, and PoBr₄ has a fcc lattice with *a*₀ = 560 pm. These compounds and PoI₄ can be made by direct combination of the

elements or indirectly, e.g. by the chlorination of PoO₂ with HCl, PCl₅ or SOCl₂, or by the reaction of PoO₂ with HI and 200°. Similar methods are used to prepare the tetrahalides of Se and Te, e.g.:



The two mixed tellurium(IV) halides listed in Table 16.5 were prepared by the action of liquid Br₂ on TeCl₂ to give the yellow solid TeBr₂Cl₂, and by the action of I₂ on TeBr₂ in ether solution to give the red crystalline TeBr₂I₂; their structures are as yet unknown.

Hexahalides

The only hexahalides known are the colourless gaseous fluorides SeF₆ and TeF₆ and the volatile

liquids TeClF_5 and TeBrF_5 . The hexafluorides are prepared by direct fluorination of the elements or by reaction of BrF_3 on the dioxides. Both are octahedral with Se-F 167–170 pm and Te-F 184 pm. SeF_6 resembles SF_6 in being inert to water but it is decomposed by aqueous solutions of KI or thiosulfate. TeF_6 hydrolyses completely within 1 day at room temperature.

The mixed halides TeClF_5 and TeBrF_5 are made by oxidative fluorination of TeCl_4 or TeBr_4 in a stream of F_2 diluted with N_2 at 25° . Under similar conditions TeI_4 gave only TeF_6 and IF_5 . TeClF_5 can also be made by the action of ClF on TeF_4 , TeCl_4 or TeO_2 below room temperature; it is a colourless liquid, mp -28° , bp 13.5° , which does not react with Hg, dry metals or glass at room temperature.

Halide complexes

It is convenient to include halide complexes in this section on the halides of Se, Te and Po and, indeed, some have already been alluded to above. In addition, pentafluoroselenates(IV) can be obtained as rather unstable white solids MSeF_5 by dissolving alkali metal fluorides or TlF in SeF_4 . The crystal structure of Me_4NSeF_5 features square-pyramidal SeF_5^- ions,⁽¹⁰⁴⁾ with $\text{Se-F}_{\text{apex}}$ 171 pm $\text{Se-F}_{\text{base}}$ 185 pm and the angle $\text{F}_a\text{-Se-F}_b$ 84° , implying that the Se atom and its lone pair of electrons lies some 20 pm below the basal plane (cf. Fig. 16.13b). The tellurium analogues are best prepared by dissolving MF and TeO_2 in aqueous HF or SeF_4 ; they are white crystalline solids. The TeF_5^- ion (like SeF_5^-) has a distorted square-based pyramidal structure (C_{4v}) in which the Te atom (and pendant lone-pair of electrons) is about 30 pm below the basal plane with $\text{Te-F}_{\text{apex}}$ 184 pm, $\text{Te-F}_{\text{base}}$ 196 pm and the angle $\text{F}_a\text{-Te-F}_b$ 81° ⁽¹⁰⁴⁾ (cf. TeF_4 , Fig. 16.13c). The resemblance to other isoelectronic $\text{MF}_5^{n\pm}$ species is illustrated in Table 16.6; in each case, the fact that the distance M-F_{base} is greater than M-F_{apex} and that the angle $\text{F}_{\text{apex}}\text{-M-F}_{\text{base}}$ is less than 90°

Table 16.6 Dimensions of some isoelectronic square-pyramidal species

Species	$\text{M-F}_{\text{apex}}/\text{pm}$	$\text{M-F}_{\text{base}}/\text{pm}$	$\angle\text{F}_{\text{apex}}\text{-M-F}_{\text{base}}$
SbF_5^{2-}	200	204	83°
TeF_5^-	184	196	81°
BrF_5	168	181	84°
XeF_5^+	181	188	79°

can be ascribed to repulsive interaction of the basal M-F bonds with the lone-pair of electrons.

Attempts to prepare compounds containing the TeF_6^{2-} ion have not been successful though numerous routes have been tried. However, reaction of Me_4NF with TeF_6 in anhydrous MeCN affords the novel 7- and 8-coordinated species TeF_7^- (D_{5h} , pentagonal bipyramid)^(105,106) and TeF_8^{2-} (D_{4d} , square antiprism),⁽¹⁰⁵⁾ There is also a remarkable heterolytic reaction of TeF_4 with 4-coordinated rhodium complexes $[\text{Rh}(\text{CO})\text{X}(\text{PEt}_3)_2]$, ($\text{X} = \text{Cl}, \text{Br}, \text{NCS}, \text{NCO}$) at -78°C to give the unusual ionic complex $[\text{Rh}(\text{CO})\text{X}(\text{PEt}_3)_2(\text{TeF}_3)]^+(\text{TeF}_5)^-$.⁽¹⁰⁷⁾ Note that the TeF_3^+ ligand is isoelectronic with PF_3 , SbF_3 , etc.

By contrast to the absence of TeF_6^{2-} , compounds of the complex anions SeX_6^{2-} and TeX_6^{2-} ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) are readily prepared in crystalline form by direct reaction (e.g. $\text{TeX}_4 + 2\text{MX}$) or by precipitating the complex from a solution of SeO_2 or TeO_2 in aqueous HX. Their most notable feature is a regular octahedral structure despite the fact that they are formally 14-electron species; it appears that with large monatomic ligands of moderate electronegativity the stereochemistry is dominated by inter-ligand repulsions and the lone-pair then either resides in an ns^2 orbital for isolated ions or is delocalized in a low-energy solid-state band.⁽¹⁰⁸⁾ Similar results

¹⁰⁵ K. O. CHRISTE, J. P. C. SANDERS, G. J. SCHROBILGEN and W. W. WILSON, *J. Chem. Soc., Chem. Commun.*, 837–40 (1991) and references cited therein.

¹⁰⁶ A. R. MAHJIOUB and K. SEPPELT, *J. Chem. Soc., Chem. Commun.*, 840–1 (1991).

¹⁰⁷ E. A. V. EBSWORTH, J. H. HOLLOWAY and P. G. WATSON, *J. Chem. Soc., Chem. Commun.*, 1443–4 (1991).

¹⁰⁸ For experimental results and theoretical discussion see I. D. BROWN, *Can. J. Chem.* **42**, 2758–67 (1964);

¹⁰⁴ A. R. MAHJIOUB, D. LEOPOLD and K. SEPPELT, *Z. anorg. allg. Chem.* **618**, 83–8 (1992).

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

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).

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

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