# 16

# Selenium, Tellurium and Polonium

## 16.1 The Elements[1-4]

### 16.1.1 Introduction: history, abundance, distribution

Tellurium was the first of these three elements to be discovered. It was isolated by the Austrian chemist F. J. Müller von Reichenstein in 1782 a few years after the discovery of oxygen by J. Priestley and C. W. Scheele (p. 600), though the periodic group relationship between the elements was not apparent until nearly a century later (p. 20). Tellurium was first observed in ores mined in the gold districts of Transylvania; Müller called it *metallum problematicum* or *aurum paradoxum* because it showed none of the properties of the expected antimony.[5] The name tellurium (Latin *tellus*, earth) is due to another Austrian chemist, M. H. Klaproth, the discoverer of zirconium and uranium.

Selenium was isolated some 35 y after tellurium and, since the new element resembled tellurium, it was named from the Greek σελήνη, *selene*, the moon. The discovery was made in 1817 by the Swedish chemist J. J. Berzelius (discoverer of Si, Ce and Th) and J. G. Gahn (discoverer of Mn);[5] they observed a reddish-brown deposit during the burning of sulfur obtained from Fahlun copper pyrites, and showed it to be volatile and readily reducible to the new element.

The discovery of polonium by Marie Curie in 1898 is a story that has been told many

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[1] K. W. BAGNALL, Selenium, tellurium and polonium, Chap. 24 in *Comprehensive Inorganic Chemistry*, Vol. 2, pp. 935–1008, Pergamon Press, Oxford, 1973.

[2] R. A. ZINGARO and W. C. COOPER (eds.), *Selenium*, Van Nostrand, Reinhold, New York, 1974, 835 pp.

[3] W. C. COOPER (ed.), *Tellurium*, Van Nostrand, Reinhold, New York, 1971, 437 pp.

[4] N. B. MIKEEV, Polonium, *Chemiker Zeitung* **102**, 277–86 (1978). See also K. W. BAGNALL, *Radiochim. Acta.* **32**, 153–61 (1983). Polonium, *Gmelin Handbook of Inorganic and Organometallic Chemistry*, Suppl. Vol. 1, Springer-Verlag, Berlin, 1990, 425 pp.

[5] M. E. WEEKS, *Discovery of the Elements*, 6th edn., Journal of Chemical Education, Easton, Pa., 1956: pp. 303–37.

times.[6] The immense feat of processing huge quantities of uranium ore and of following the progress of separation by the newly discovered phenomenon of radioactivity (together with her parallel isolation of radium by similar techniques, p. 108), earned her the Nobel Prize for Chemistry in 1911. She had already shared the 1902 Nobel Prize for Physics with H. A. Becquerel and her husband P. Curie for their joint researches on radioactivity. Indeed, this was the first time, though by no means the last, that invisible quantities of a new element had been identified, separated, and investigated solely by means of its radioactivity. The element was named after Marie Curie's home country, Poland.

Selenium and tellurium are comparatively rare elements, being sixty-sixth and seventy-third respectively in order of crustal abundance; polonium, on account of its radioactive decay, is exceedingly unabundant. Selenium comprises some 0.05 ppm of the earth's crust and is therefore similar to Ag and Hg, which are each about 0.08 ppm, and Pd (0.015 ppm). Tellurium, at about 0.002 ppm can be compared with Au (0.004 ppm) and Ir (0.001 ppm). Both elements are occasionally found native, in association with sulfur, and many of their minerals occur together with the sulfides of chalcophilic metals (p. 648),[2,3] e.g. Cu, Ag, Au; Zn, Cd, Hg; Fe, Co, Ni; Pb, As, Bi. Sometimes the minerals are partly oxidized, e.g. $MSeO_3.2H_2O$ (M = Ni, Cu, Pb); $PbTeO_3$, $Fe_2(TeO_3)_3.2H_2O$, $FeTeO_4$, $Hg_2TeO_4$, $Bi_2TeO_4(OH)_4$, etc. Selenolite, $SeO_2$, and tellurite, $TeO_2$, have also been found.

Polonium has no stable isotopes, all 27 isotopes being radioactive; of these only $^{210}$Po occurs naturally, as the penultimate member of the radium decay series:

$$^{210}_{82}\text{Pb} \xrightarrow[22.3 \text{ y}]{\beta^-} {}^{210}_{83}\text{Bi} \xrightarrow[5.01 \text{ d}]{\beta^-} {}^{210}_{84}\text{Po} \xrightarrow[138.38 \text{ d}]{\alpha} {}^{206}_{82}\text{Pb}$$

$$\text{RaD} \qquad\qquad \text{RaE} \qquad\qquad \text{RaF} \qquad\qquad \text{RaG}$$

Because of the fugitive nature of $^{210}$Po, uranium ores contain only about 0.1 mg Po per tonne of ore (i.e. $10^{-4}$ ppm). The overall abundance of Po in crustal rocks of the earth is thus of the order of $3 \times 10^{-10}$ ppm.

## 16.1.2 Production and uses of the elements [2-4,7]

The main source of Se and Te is the anode slime deposited during the electrolytic refining of Cu (p. 1175); this mud also contains commercial quantities of Ag, Au and the platinum metals. Direct recovery from minerals is not usually economically viable because of their rarity. Selenium is also recovered from the sludge accumulating in sulfuric acid plants and from electrostatic precipitator dust collected during the processing of Cu and Pb. Detailed procedures for isolation and purification depend on the relative concentrations of Se, Te and other impurities, but a typical sequence involves oxidation by roasting in air with soda ash followed by leaching:

$$Ag_2Se + Na_2CO_3 + O_2 \xrightarrow{650°}$$
$$2Ag + Na_2SeO_3 + CO_2$$

$$Cu_2Se + Na_2CO_3 + 2O_2 \longrightarrow$$
$$2CuO + Na_2SeO_3 + CO_2$$

$$Cu_2Te + Na_2CO_3 + 2O_2 \longrightarrow$$
$$2CuO + Na_2TeO_3 + CO_2$$

In the absence of soda ash, $SeO_2$ can be volatilized directly from the roast:

$$Cu_2Se + \tfrac{3}{2}O_2 \xrightarrow{300°} CuO + CuSeO_3 \xrightarrow{650°}$$
$$2CuO + SeO_2$$

$$Ag_2SeO_3 \xrightarrow{700°} 2Ag + SeO_2 + \tfrac{1}{2}O_2$$

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[6] Ref. 5, Chap. 29, pp. 803–43. See also E. FARBER, *Nobel Prize Winners in Chemistry 1901–1961*, Abelard-Schuman, London, Marie Sklodowska Curie, pp. 45–8. F. C. WOOD, Marie Curie, in E. FARBER (ed.), *Great Chemists*, pp. 1263–75. Interscience, New York, 1961.

[7] *Kirk–Othmer Encyclopedia of Chemical Technology*, 4th edn., 1997, Selenium and Selenium Compounds, Vol. 21, pp. 686–719, Tellurium and tellurium compounds, Vol. 22, pp. 659–79, 1983.

Separation of Se and Te can also be achieved by neutralizing the alkaline selenite and tellurite leach with $H_2SO_4$; this precipitates the tellurium as a hydrous dioxide and leaves the more acidic selenous acid, $H_2SeO_3$, in solution from which 99.5% pure Se can be precipitated by $SO_2$:[†]

$$H_2SeO_3 + 2SO_2 + H_2O \longrightarrow Se + 2H_2SO_4$$

Tellurium is obtained by dissolving the dioxide in aqueous NaOH followed by electrolytic reduction:

$$Na_2TeO_3 + H_2O \longrightarrow Te + 2NaOH + O_2$$
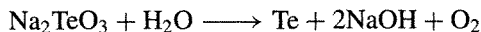
The NaOH is regenerated and only make-up quantities are required. However, the detailed processes adopted industrially to produce Se and Te are much more complex and sophisticated than this outline implies.[(2,3,7)]

World production of refined Se in 1995 was ~2000 tonnes the largest producers being Japan (600 t), USA (360 t) and Canada (300 t). The pattern of use no doubt varies somewhat from country to country, but in the USA the largest single use of the element (35%) is as a decolorizor of glass (0.01–0.15 kg/tonne). Higher concentrations (1–2 kg/tonne) yield delicate pink glasses. The glorious selenium ruby glasses, which are the most brilliant reds known to glass-makers, are obtained by incorporating solid particles of cadmium sulfoselenide in the glass; the deepest ruby colour is obtained when Cd(S,Se) has about 10% CdS, but as the relative concentration of CdS increases the colour moderates to red (40% CdS), orange (75%) and yellow (100%). Cadmium sulfoselenides are also widely used as heat-resistant red pigments in plastics, paints, inks and enamels. Another very important application of elemental Se is in xerography, which has developed during the past four decades into the pre-eminent process for document copying, as witnessed by the ubiquitous presence of xerox machines in offices and libraries (see Panel). Related uses are as a photoconductor (selenium photoelectric cells) and as a rectifier in semiconductor devices (p. 258). Small amounts of ferroselenium are used to improve the casting, forging and machinability of stainless steels, and the dithiocarbamate $[Se(S_2CNEt_2)_4]$ finds some use in the processing of natural and synthetic rubbers. Selenium pharmaceuticals comprise a further small outlet. In addition to Se, Fe/Se, Cd(S,Se) and $[Se(S_2CNEt_2)_4]$ the main commercially available compounds of Se are $SeO_2$, $Na_2SeO_3$, $Na_2SeO_4$, $H_2SeO_4$ and $SeOCl_2$ (q.v.).

Production of Te is on a much smaller scale: *ca.* 350 tonnes in 1978, dominated by USA, Canada and Japan. More than 70% of the Te is used in iron and steel production and in non-ferrous metals and alloys, and 25% for chemicals. A small amount of $TeO_2$ is used in tinting glass, and Te compounds find some use as catalysts and as curing agents in the rubber industry. In addition to Te, Fe/Te and $TeO_2$, commercially important compounds include $Na_2TeO_4$ and $[Te(S_2CNEt_2)_4]$.

Polonium, because of its very low abundance and very short half-life, is not obtained from natural sources. Virtually all our knowledge of the physical and chemical properties of the element come from studies on $^{210}$Po which is best made by neutron irradiation of $^{209}$Bi in a nuclear reactor:

$$^{209}_{83}Bi(n,\gamma)^{210}_{83}Bi \xrightarrow[t_{\frac{1}{2}}5.01\ d]{\beta^-} {}^{210}_{84}Po \xrightarrow[t_{\frac{1}{2}}138.38\ d]{\alpha} \cdots$$
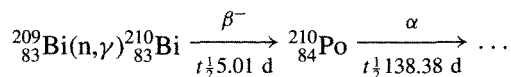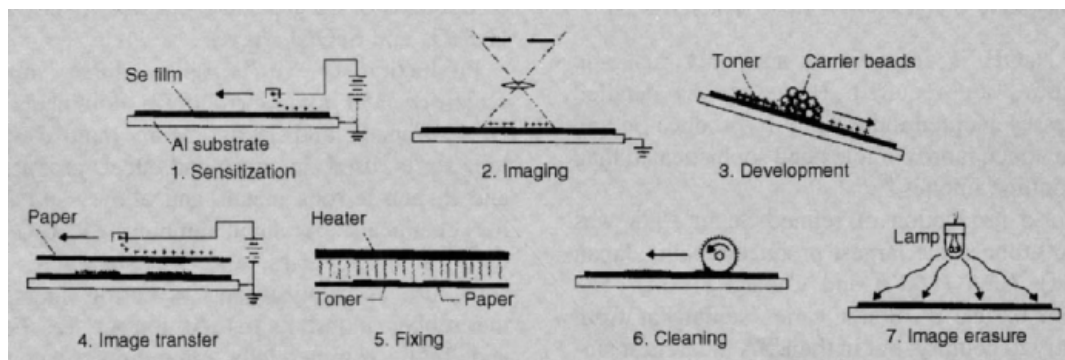
It will be recalled that $^{209}$Bi is 100% abundant and is the heaviest stable nuclide of any element (p. 550), but it is essential to use very high purity Bi to prevent unwanted nuclear side-reactions which would contaminate the product $^{210}$Po; in particular Sc, Ag, As, Sb and Te must be <0.1 ppm and Fe <10 ppm. Polonium can be obtained directly in milligram amounts by fractional vacuum distillation from the metallic bismuth. Alternatively, it can be deposited spontaneously by electrochemical replacement onto the surface of a less electropositive metal

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[†] Very pure Se can be obtained by heating the crude material in $H_2$ at 650° and then decomposing the $H_2Se$ so formed by passing the gas through a silica tube at 1000°. Any $H_2S$ present, being more stable than $H_2Se$, passes through the tube unchanged, whereas hydrides which are less stable than $H_2Se$, such as those of Te, P, As, Sb, are not formed in the initial reaction at 650°.

## Xerography

The invention of xerography by C. F. Carlson (USA) in the period 1934–42 was the culmination of a prolonged and concerted attack on the problem of devising a rapid, cheap and dry process for direct document copying without the need for the intermediate formation of a permanent photographic "negative", or even the use of specially prepared photographic paper for the "print". The discovery that vacuum-deposited amorphous or vitreous selenium was the almost ideal photoconductor for xerography was made in the Battelle Memorial Institute (Ohio, USA) in 1948. The dramatic success of these twin developments is witnessed by the vast number of xerox machines in daily use throughout the world today. However, early xerox equipment was not automatic. Models introduced in 1951 became popular for making offset masters, and rotary xerographic machines were introduced in 1959, but it was only after the introduction of the Xerox 914 copier in the early 1960s that electrophotography came of age. The word "xerography" derives from the Greek ξηρό, *xero* dry, γραφή, *graphy*, writing.

The sequential steps involved in commercial machines which employ reusable photoreceptors for generating xerox copies are shown in the figure[2] and further elucidated below.



1. Sensitization       2. Imaging       3. Development       4. Image transfer       5. Fixing       6. Cleaning       7. Image erasure

1. *Sensitization of the photoreceptor.* The photoreceptor consists of a vacuum-deposited film of amorphous Se, $\sim$50 μm thick, on an Al substrate; this is sensitized by electrostatic charging from a corona discharge using a field of $\sim$10$^5$ V cm$^{-1}$.

2. *Exposure and latent image formation.* The sensitized photoreceptor is exposed to a light and dark image pattern; in the light areas the surface potential of the photoconductor is reduced due to a photoconductive discharge. Since current can only flow perpendicular to the surface, this step produces an electrostatic-potential distribution which replicates the pattern of the image.

3. *Development of the image.* This is done using a mixture of black (or coloured) toner particles, typically 10 μm in diameter, and spherical carrier beads ($\sim$100 μm diameter). The toner particles become charged triboelectrically (i.e. by friction) and are preferentially attracted either by the surface fringe field at light–dark boundaries or (in systems with a developing electrode) by the absolute potential in the dark areas; they adhere to the photoreceptor, thus forming a visible image corresponding to the latent electrostatic image.

4. *Image transfer.* This is best done electrostatically by charging the print paper to attract the toner particles.

5. *Print fixing.* The powder image is made permanent by fusing or melting the toner particles into the surface of the paper, either by heat, by heat and pressure, or by solvent vapours.

6. *Cleaning.* Any toner still left on the photoreceptor after the transfer process is removed with a cloth web or brush, or by a combination of electrostatic and mechanical means.

7. *Image erasure.* The potential differences due to latent image formation are removed by flooding the photoreceptors with a sufficiently intense light source to drive the surface potential to some uniformly low value (typically $\sim$100 V corresponding to fields of $\sim$10$^4$ V cm$^{-1}$); the photoreceptor is then ready for another print cycle.

The elegance, cheapness and convenience of xerography for document copying has led to rapid commercial development on a colossal scale throughout the world.

such as Ag. Solution techniques are unsuitable except on the trace scale (submicrogram amounts) because of the radiation damage caused by the intense radioactivity (p. 753). All

applications of Po depend on its radioactivity: it is an almost pure $\alpha$-emitter ($E_\alpha$ 5.30 MeV) and only 0.0011% of the activity is due to $\gamma$-rays ($E_{max}$ 0.803 MeV). Because of its short

half-life (138.38 d) this entails a tremendous energy output of 141 W per gram of metal: in consequence, there is considerable self-heating of Po and its compounds. The element can therefore be used as a convenient light-weight heat source, or to generate spontaneous and reliable thermoelectric power for space satellites and lunar stations, since no moving parts are involved. Polonium also finds limited use as a neutron generator when combined with a light element of high $\alpha,n$ cross-section such as beryllium: $^9_4Be(\alpha,n)^{12}_6C$. The best yield (93 neutrons per $10^6\alpha$-particles) is obtained with a BeO target.

## 16.1.3 Allotropy

At least eight structurally distinct forms of Se are known: the three red monoclinic polymorphs ($\alpha$, $\beta$ and $\gamma$) consist of $Se_8$ rings and differ only in the intermolecular packing of the rings in the crystals. Other ring sizes have recently been synthesized in the red allotropes cyclo-$Se_6$ and cyclo-$Se_7$, and the heterocyclic analogues cyclo-$Se_5S$ and cyclo-$Se_5S_2$.[8] The grey, "metallic", hexagonal crystalline form features helical polymeric chains and these also occur, somewhat deformed, in amorphous red Se. Finally, vitreous black Se, the ordinary commercial form of the element, comprises an extremely complex and irregular structure of large polymeric rings having up to 1000 atoms per ring.

The $\alpha$- and $\beta$-forms of red crystalline $Se_8$ are obtained respectively by the slow and rapid evaporation of $CS_2$ or benzene solutions of black vitreous Se and more recently a third ($\gamma$) form of red crystalline $Se_8$ was obtained from the reaction of dipiperidinotetraselane with solvent $CS_2$:[9]

$$[Se_4(NC_5H_{10})_2] \xrightarrow{2CS_2} [Se(S_2CNC_5H_{10})_2] + \tfrac{3}{8}Se_8$$
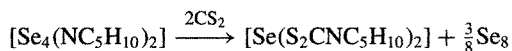
All three allotropes consist of almost identical puckered $Se_8$ rings similar to those found in cyclo-$S_8$ (p. 658) and of average dimensions Se–Se 233.5 pm, angle Se–Se–Se 105.7°, dihedral angle 101.3° (Fig. 16.1a). The intermolecular packing is most efficient for the $\alpha$-form. [It is interesting to note that $\beta$-$Se_8$ was at one time thought, on the basis of an X-ray crystal structure determination, to be an 8-membered chain with the configuration of a puckered ring in which 1 Se-Se bond had been broken; the error was corrected in a very perceptive paper by L. Pauling and his co-workers.[10]] Both $\alpha$- and $\beta$-$Se_8$ (and presumably also $\gamma$-$Se_8$) are appreciably soluble in $CS_2$ to give red solutions.

Grey, hexagonal, "metallic" selenium is thermodynamically the most stable form of the element and can be formed by warming other modifications; it can also be obtained by slowly cooling molten Se or by condensing Se vapour at a temperature just below the mp (220.5°). It is a photoconductor (p. 750) and is the only modification which conducts electricity. The structure (Fig. 16.1b) consists of unbranched helical chains with Se–Se 237.3 pm, angle Se–Se–Se 103.1°, and a repeat unit every 3 atoms (cf. fibrous sulfur, p. 660). The closest Se $\cdots$ Se distance between chains is 343.6 pm, which is very close to that in $Te_x$ (350 pm) (see below). Grey $Se_x$ is insoluble in $CS_2$ and its density, 4.82 g cm$^{-3}$, is the highest of any modification of the element. A related allotrope is red amorphous Se, formed by condensation of Se vapour onto a cold surface or by precipitation from aqueous solutions of selenous acid by treatment with $SO_2$ (p. 755) or other reducing agents such as hydrazine hydrate. It is slightly soluble in $CS_2$, and has a deformed chain structure but does not conduct electricity. The heat of transformation to the stable hexagonal

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[8] R. STEUDEL and E.-M. STRAUSS, in H. J. EMELÉUS and A. G. SHARPE, Adv. Inorg. Chem. Radiochem. **28**, 135–66 (1984). R. STEUDEL, M. PAPAVASSILIOU, E.-M. STRAUSS and R. LAITINEN, Angew. Chem. Int. Edn. Engl. **25**, 99–101 (1986) and references cited therein. See also R. STEUDEL and M. PAPAVASSILIOU, Polyhedron **7**, 581–3 (1988), R. STEUDEL, M. PRIDÖHL, H. HARTL and I. BRÜGAM, Z. anorg. allg. Chem. **619**, 1589–96 (1993).

[9] O. FOSS and V. JANICKIS, J. Chem. Soc., Chem. Commun., 834–5 (1977).

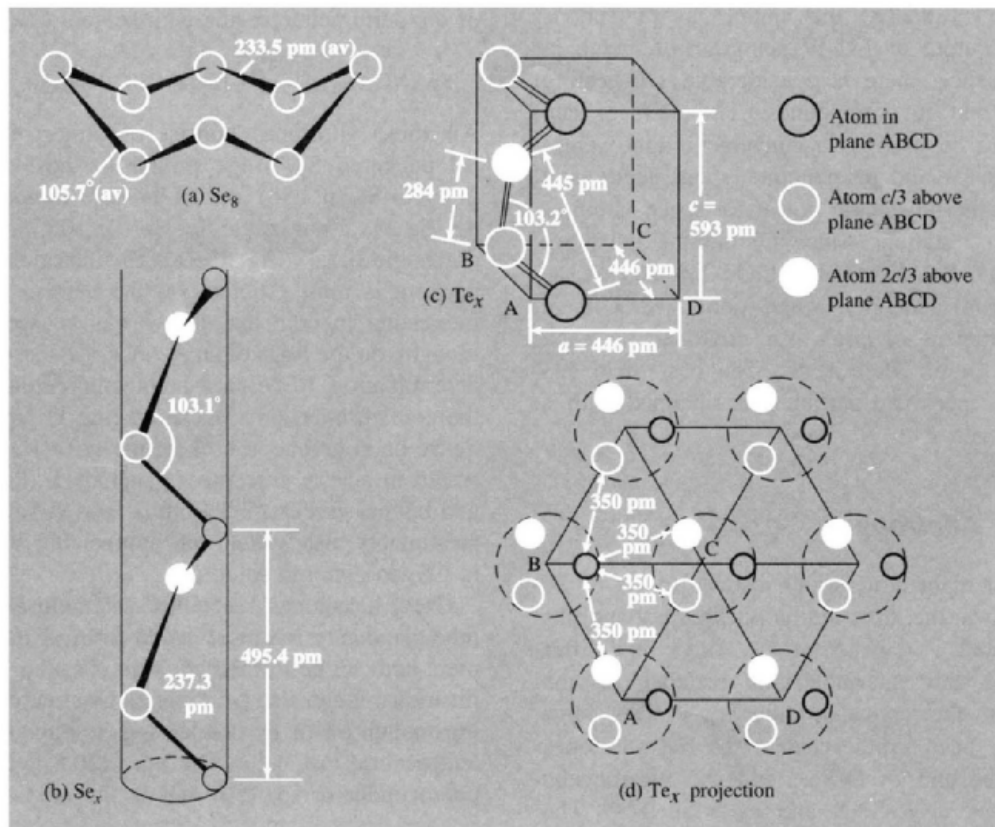[10] R. E. MARSH, L. PAULING and J. D. MCCULLOUGH, Acta Cryst. **6**, 71–5 (1953).

**Figure 16.1**   Structures of various allotropes of selenium and the structure of crystalline tellurium: (a) the $Se_8$ unit in $\alpha$- $\beta$- and $\gamma$-red selenium; (b) the helical Se chain along the $c$-axis in hexagonal grey selenium; (c) the similar helical chain in crystalline tellurium shown in perspective; and (d) projection of the tellurium structure on a plane perpendicular to the $c$-axis.

grey form has been variously quoted but is in the region of $5-10$ kJ per mole of Se atoms.

Vitreous, black Se is the ordinary commercial form of the element, obtained by rapid cooling of molten Se; it is a brittle, opaque, bluish-black lustrous solid which is somewhat soluble in $CS_2$. It does not melt sharply but softens at about 50° and rapidly transforms to hexagonal grey Se when heated to 180° (or at lower temperatures when catalysed by halogens, amines, etc.). There has been much discussion about the structure but it seems to comprise rings of varying size up to quite high molecular weights. Presumably these rings cleave and polymerize into helical chains under the influence of thermal soaking or

catalysts. The great interest in the various allotropes of selenium and their stabilization or interconversion, stems from its use in photocells, rectifiers, and xerography (p. 750).[2]

Tellurium has only one crystalline form and this is composed of a network of spiral chains similar to those in hexagonal Se (Fig. 16.1c and d). Although the intra-chain Te–Te distance of 284 pm and the $c$ dimension of the crystal (593 pm) are both substantially greater than for $Se_x$ (as expected), nevertheless the closest inter-atomic distance between chains is almost identical for the 2 elements ($Te \cdots Te$ 350 pm). Accordingly the elements form a continuous range of solid solutions in which there is a random

**Table 16.1**  Production and properties of long-lived Po isotopes

| Isotope | Production | $t_{\frac{1}{2}}$ | $E_\gamma$/MeV | $A_r$ (relative atomic mass) |
|---------|-----------|------|-------|------------|
| $^{208}$Po | $^{209}$Bi(d,3n) or (p,2n) | 2.898 y | 5.11 | 207.9812 |
| $^{209}$Po | $^{209}$Bi(d,2n) or (p,n) | 102 y | 4.88 | 208.9824 |
| $^{210}$Po | $^{209}$Bi(n,$\gamma$) | 138.376 d | 5.305 | 209.9828 |

alternation of Se and Te atoms in the helical chains.[11] The homogeneous alloys Se$_x$Te$_{1-x}$ can also, most remarkably, be prepared directly by hydrazine reduction of glycol solutions of $x$SeO$_2$ and $(1-x)$TeO$_2$ or other compounds of Se$^{IV}$ and Te$^{IV}$ such as dialkylselenites and tetraalkoxytelluranes); the lattice parameters and mp of the alloys vary steadily between those of the two end members Se and Te.[12] The rapid diminution in allotropic complexity from sulfur through selenium to tellurium is notable.

Polonium is unique in being the only element known to crystallize in the simple cubic form (6 nearest neighbours at 335 pm). This $\alpha$-form distorts at about 36° to a simple rhombohedral modification in which each Po also has 6 nearest neighbours at 335 pm. The precise temperature of the phase change is difficult to determine because of the self-heating of crystalline Po (p. 751) and it appears that both modifications can coexist from about 18° to 54°. Both are silvery-white metallic crystals with substantially higher electrical conductivity than Te.

## 16.1.4 Atomic and physical properties

Selenium, Te and Po are the three heaviest members of Group 16 and, like their congenors O and S, have two p electrons less than the next following noble gases. Selenium is normally said to have 6 stable isotopes though the heaviest of these ($^{82}$Se, 8.73% abundant) is actually an extremely long-lived $\beta^-$ emitter,

$t_{\frac{1}{2}}$ $1.4 \times 10^{20}$ y. The most abundant isotope is $^{80}$Se (49.61%), and all have zero nuclear spin except the 7.63% abundant $^{77}$Se $(I = \frac{1}{2})$, which is finding increasing use in nmr experiments.[13] Because of the plethora of isotopes the atomic weight is only known to about 1 part in 2600 (p. 16). Tellurium, with 8 naturally occurring stable isotopes, likewise suffers some imprecision in its atomic weight (1 part in 4300). The most abundant isotopes are $^{130}$Te (33.87%) and $^{128}$Te (31.70%), and again all have zero nuclear spin except the nmr active isotopes $^{123}$Te (0.905%) and $^{125}$Te (7.12%), which have spin $\frac{1}{2}$.[13] $^{125}$Te also has a low-lying nuclear isomer $^{125m}$Te which decays by pure $\gamma$ emission ($E_\gamma$ 35.48 keV, $t_{\frac{1}{2}}$ 58 d) — this has found much use in Mössbauer spectroscopy.[14] Polonium, as we have seen (p. 748), has no stable isotopes. The 3 longest lived, together with their modes of production and other properties, are as shown in Table 16.1.

Several atomic and physical properties of the elements are given in Table 16.2. The trends to larger size, lower ionization energy and lower electronegativity are as expected. The trend to metallic conductivity is also noteworthy; indeed, Po resembles its horizontal neighbours Bi, Pb and Tl not only in this but in its moderately high density and notably low mp and bp.

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[11] A. A. KUDRYAVTSEV, *The Chemistry and Technology of Selenium and Tellurium*, Collet's Publishers, London, 1974, 278 pp.

[12] T. W. SMITH, S. D. SMITH and S. S. BADESHA, *J. Am. Chem. Soc.* **106**, 7247–8 (1984).

[13] C. RODGER, N. SHEPPARD, H. C. E. McFARLANE, and W. McFARLANE, in R. K. HARRIS and B. R. MANN (eds.), *NMR and the Periodic Table*, pp. 402–19. Academic Press, London, 1978. H. C. E. McFARLANE and W. McFARLANE, in J. MASON (ed.) *Multinuclear NMR* pp. 417–35, Plenum Press, New York, 1987.

[14] N. N. GREENWOOD and T. C. GIBB, *Mössbauer Spectroscopy*, pp. 452–62, Chapman & Hall, London, 1971. F. J. BERRY, Chap. 8 in G. J. LONG (ed.) *Mössbauer Spectroscopy Applied to Inorganic Chemistry*, Vol. 2, Plenum Press, New York 1987, pp. 343–90.

**Table 16.2** Some atomic and physical properties of selenium, tellurium and polonium

| Property | Se | Te | Po |
|---|---|---|---|
| Atomic number | 34 | 52 | 84 |
| Number of stable isotopes | 6 | 8 | 0 |
| Electronic structure | $[Ar]3d^{10}4s^24p^4$ | $[Kr]4d^{10}5s^25p^4$ | $[Xe]4f^{14}5d^{10}6s^26p^4$ |
| Atomic weight | 78.96($\pm$ 0.03) | 127.60($\pm$ 0.03) | (210) |
| Atomic radius (12-coordinate)/pm[a] | 140[a] | 160[a] | 164[a] |
| Ionic radius/pm ($M^{2-}$) | 198 | 221 | (230?) |
| ($M^{4+}$) | 50 | 97 | 94 |
| ($M^{6+}$) | 42 | 56 | 67 |
| Ionization energy/kJ mol$^{-1}$ | 940.7 | 869.0 | 813.0 |
| Pauling electronegativity | 2.4 | 2.1 | 2.0 |
| Density(25°)/g cm$^{-3}$) | Hexag 4.189 | 6.25 | $\alpha$9.142 |
| | $\alpha$-monoclinic 4.389 | | $\beta$9.352 |
| | Vitreous 4.285 | | |
| MP/°C | 217 | 452 | 246–254 |
| BP/°C | 685 | 990 | 962 |
| $\Delta H_{atomization}$/kJ mol$^{-1}$ | 206.7 | 192 | — |
| Electrical resistivity(25°)/ohm cm | $10^{10[b]}$ | 1 | $\alpha 4.2 \times 10^{-5}$ |
| | | | $\beta 4.4 \times 10^{-5}$ |
| Band energy gap $E_g$/kJ mol$^{-1}$ | 178 | 32.2 | 0 |

[a]The 2-coordinate covalent radius is 119 pm for elemental Se and 142 pm for Te; the 6-coordinate metallic radius of Po is 168 pm.

[b]Depends markedly on purity, temperature and photon flux; resistivity of liquid Se at 400° is $1.3 \times 10^5$ ohm cm.

### 16.1.5 Chemical reactivity and trends

The elements in Group 16 share with the preceding main-group elements the tendency towards increasing metallic character as the atomic weight increases within the group. Thus O and S are insulators, Se and Te are semiconductors and Po is a metal. Parallel with this trend is the gradual emergence of cationic (basic) properties with Te, and these are even more pronounced with Po. For example, Se is not appreciably attacked by dilute HCl whereas Te dissolves to some extent in the presence of air; Po dissolves readily to yield pink solutions of Po$^{II}$ which are then rapidly oxidized further to yellow Po$^{IV}$ by the products of radiolytic decomposition of the solvent. Likewise, the structure and bonding of the halides of these elements depends markedly on both the electronegativity of the halogen and on the oxidation state of the central element, thereby paralleling the "ionic-covalent" transition which has already been discussed for the halides of P (p. 499), As and Sb (p. 558), and S (p. 691).

Selenium, Te and Po combine directly with most elements, though less readily than do O and S. The most stable compounds are (a) the selenides, tellurides and polonides ($M^{2-}$) formed with the strongly positive elements of Groups 1, 2 and the lanthanides, and (b) the compounds with the electronegative elements O, F and Cl in which the oxidation states are +2, +4 and +6. The compounds tend to be less stable than the corresponding compounds of S (or O), and there are few analogues of the extensive range of sulfur–nitrogen compounds (p. 721). A similar trend (also noted in the preceding groups) is the decreasing thermal stability of the hydrides: $H_2O > H_2S > H_2Se > H_2Te > H_2Po$. Selenium and tellurium share to a limited extent sulfur's great propensity for catenation (see allotropy of the elements, polysulfanes, halides, etc.).

As found in preceding groups, there is a diminution in the stability of multiple bonds (e.g. to C, N, O) and a corresponding decrease in their occurrence as the atomic number of the group element increases. Thus O=C=O and (to a lesser extent) S=C=S are stable, whereas

$Se=C=Se$ polymerizes readily, $Se=C=Te$ is unstable and $Te=C=Te$ is unknown. Again, $SO_2$ is a (nonlinear) gaseous molecule, $\overset{S}{\underset{O \quad O}{\diagup\diagdown}}$, whereas $SeO_2$ is a chain polymer $-O-Se(=O)-$ (p. 779) and $TeO_2$ features 4-coordinate pseudo-trigonal-bipyramidal units $\{:TeO_4\}$ which are singly-bonded into extended layer or 3D structures (p. 779); in $PoO_2$ the coordination number increases still further to 8 and the compound adopts the typical "ionic" fluorite structure (p. 118). It can be seen that double bonds are less readily formed between 2 elements the greater the electronegativity difference between them and the smaller the sum of their individual electronegativities; this is paralleled by a diminution in double-bond formation with increasing size of the more electropositive element and the consequent decrease in bond energy.

The redox properties of the elements also show interesting trends. In common with several elements immediately following the first (3d) transition series (especially Ge, As, Se, Br) selenium shows a marked resistance to oxidation up to its group valency, i.e. $Se^{VI}$. For example, whereas $HNO_3$ readily oxidizes S to $H_2SO_4$, selenium gives $H_2SeO_3$. Again dehydration of $H_2SO_4$ with $P_2O_5$ yields $SO_3$ whereas $H_2SeO_4$ gives $SeO_2 + \frac{1}{2}O_2$. Likewise S forms a wide range of sulfones, $R_2SO_2$, but very few selenones are known; thus, $Ph_2SeO$ is not oxidized either by $HNO_3$ or by acidified $K_2Cr_2O_7$, and alkaline $KMnO_4$ is required to produce $Ph_2SeO_2$ (mp 155°). As noted in the isolation of the element (p. 749), $SO_2$ precipitates Se from acidified solutions of $Se^{IV}$.

The standard reduction potentials of the elements in acid and alkaline solutions are summarized in the schemes below.[15] It is

[15] A. J. BARD, R. PARSONS and J. JORDAN, (eds.) *Standard Potentials in Aqueous Solution*, (IUPAC) Marcel Dekker, New York, 1985, 834 pp.
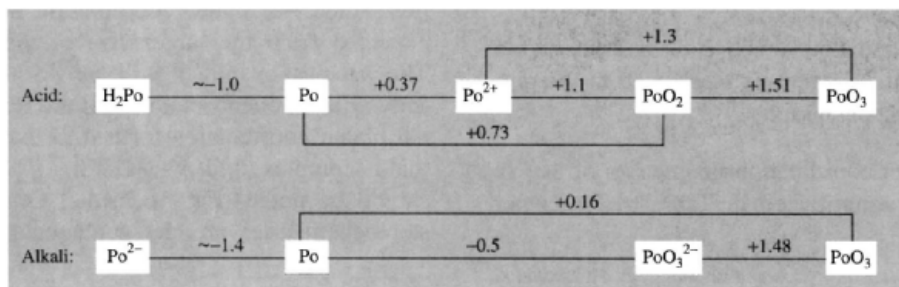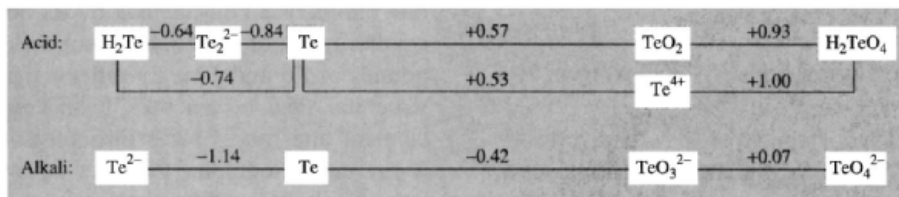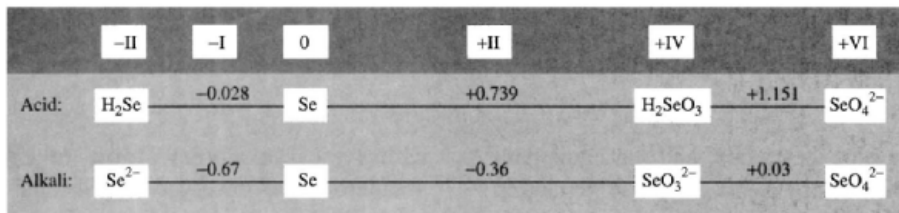


Standard reduction potentials of Se, Te and Po.[15]

**Table 16.3** Coordination geometries of selenium, tellurium and polonium

| Coordination number | Se | Te | Po |
|---|---|---|---|
| 1 | COSe, CSe$_2$, NCSe$^-$, MoSe$_4$$^{2-}$, WSe$_4$$^{2-}$ | COTe, CSTe Te$_3$$^{2-}$ | |
| 2 (bent) | Se$_x$, H$_2$Se, R$_2$Se cyclo-Se$_4$$^{2+}$ | Te$_x$, H$_2$Te, R$_2$Te, TeBr$_2$ cyclo-Te$_4$$^{2+}$ | |
| (linear) | [L$_n$Cr≡Se≡CrL$_n$]$^{(a)}$ | | |
| 3 (trigonal planar) | [(L$_n$Cr)$_3$($\mu_3$-Se)]$^{-(a)}$ | TeO$_3$(g) | |
| (pyramidal) | (SeO$_2$)$_x$, SeOX$_2$, SeMe$_3$$^+$ | TeO$_3$$^{2-}$, TeMe$_3$$^+$ | |
| 4 (planar) | — | [TeBr$_2${SC(NH$_2$)$_2$}$_2$] | |
| (tetrahedral) | SeO$_4$$^{2-}$, SeO$_2$Cl$_2$ | — | CdPo (ZnS) |
| (pseudo-trigonal bipyramidal) | R$_2$SeX$_2$ | TeO$_2$, Me$_2$TeCl$_2$ | |
| 5 (square pyramidal) | [SeOCl$_2$py$_2$] | TeF$_5$$^-$, [TeI$_4$Me]$^+$ | |
| (pentagonal planar) | — | [Te(S$_2$COEt)$_3$]$^-$ (Fig. 16.2a) | |
| 6 (octahedral) | SeF$_6$, SeBr$_6$$^{2-}$ | Te(OH)$_6$, TeBr$_6$$^{2-}$ | PoI$_6$$^{2-}$, Po metal CaPo (NaCl) |
| (trigonal prismatic) | VSe, CrSe, MnSe (NiAs) | ScTe, VTe, MnTe, (NiAs) | MgPo (NiAs) |
| (pentagonal pyramidal) | — | [Me Te(I){S$_2$CNEt$_2$}$_2$] (Fig. 16.2b) | |
| 7 (pentagonal bipyramidal) | — | [PhTe{S$_2$CNEt$_2$}$_2$-{S$_2$P(OEt)$_2$}] (Fig. 16.2c) | |
| 8 (cubic) | — | TeF$_8$$^{2-}$(?) | Na$_2$Po, PoO$_2$ (CaF$_2$) |

$^{(a)}${CrL$_n$} = {Cr($\eta^5$-C$_5$H$_5$)(CO)$_2$}$^{(16)}$

instructive to plot these data, and the equivalent values for sulfur, as volt-equivalents *vs* oxidation state (pp. 435–8), when the following trends (in acid solution) become obvious:

   (i) the decreasing stability of H$_2$M from H$_2$S to H$_2$Po;

   (ii) the greater stability of M$^{IV}$ relative to M$^0$ and M$^{VI}$ for Se, Te and Po (but not for S, p. 706), as shown by the concavity of the graph;

   (iii) the anomalous position of Se in its higher oxidation states, as mentioned in the preceding paragraph.

The known coordination geometries of Se, Te and Po are summarized in Table 16.3 together with typical examples. Most of the common geometries are observed for Se and Te, though twofold (linear) is rare and fivefold (trigonal bipyramidal) is conspicuous by its absence. The smaller range of established geometries for compounds of Po undoubtedly reflects the paucity of structural data occasioned by the rarity of this element and the extreme difficulty of obtaining X-ray crystallographic or other structural information. There appears, however, to be a clear preference for higher coordination numbers, as expected from the larger size of the Po atom. The various examples will be discussed more fully in subsequent sections but the rare pentagonal planar coordination formed in the ethyl xanthato complex [Te($\eta^2$-S$_2$COEt)$_2$($\eta^1$-S$_2$COEt)]$^-$ should be noted (Fig. 16.2a);$^{(17)}$ Other unusual stereochemistries are the pentagonal pyramidal

$^{16}$ W. A. HERRMANN, J. ROHRMANN, E. HERDTWECK, H. BOCK and A. VELTMANN, *J. Am. Chem. Soc.* **108**, 3134–5 (1986).

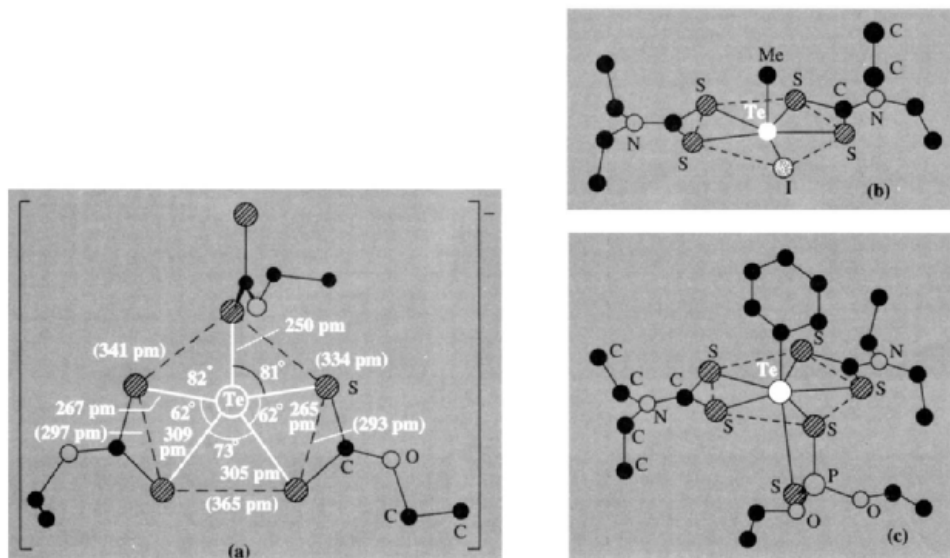$^{17}$ B. F. HOSKINS and C. D. PANNAN, *J. Chem. Soc., Chem. Commun.*, 408–9 (1975).

**Figure 16.2**   Structure of (a) the anion $[Te(S_2COEt)_3]^-$, the first authentic example of 5-coordinate pentagonal planar geometry;[17] (b) $[MeTe(I)\{S_2CNEt_2\}_2]$[18] and (c) $[PhTe\{S_2CNEt_2\}_2\{S_2P(OEt)_2\}]$[18] (see text).

6-coordinate $Te^{IV}$ in $[MeTe(I)\{S_2CNEt_2\}_2]$[18] and pentagonal bipyramidal 7-coordinate $Te^{IV}$ in $[PhTe\{S_2CNEt_2\}_2\{S_2P(OEt)_2\}]$;[18] in both cases the crystallographic data suggest the presence of a stereochemically active lone pair of electrons which distorts the regular geometry of the coordination sphere. This structure is consistent with a pentagonal bipyramidal set of orbitals on $Te^{II}$, 2 of which are occupied by stereochemically active lone-pairs directed above and below the $TeS_5$ plane. By contrast, the single lone-pairs in $Se^{IV}X_6^{2-}$, $Te^{IV}X_6^{2-}$ and $Po^{IV}I_6^{2-}$ are sterically inactive and the 14-(valence)electron anions are accurately octahedral (see p. 776), as in molecular $Se^{VI}F_6$, which has only 12 valence electrons.

Other less-symmetrical coordination geometries for Se and Te occur in the $\mu$-$Se_2$ and $\mu$-$Te_2$ complexes and the polyatomic cluster cations $Se_{10}^{2+}$ and $Te_6^{4+}$, as mentioned below.

The coordination chemistry of complexes in which Se is the donor atom has been extensively studied.[2,19] Ligands with Te as donor atom have been less widely investigated but both sets of ligands resemble $S$-donor ligands (p. 673) rather than $O$-donor ligands in favouring b-class acceptors such as $Pd^{II}$, $Pt^{II}$ and $Hg^{II}$. The linear selenocyanate ion $SeCN^-$, like the thiocyanate ion (p. 324) is ambidentate, bonding via Se to heavy metals and via N (isoselenocyanate) to first-row transition metals, e.g. $[Ag^I(SeCN)_3]^{2-}$, $[Cd^{II}(SeCN)_4]^{2-}$ $[Pb^{II}(SeCN)_6]^{4-}$, but $[Cr^{III}(NCSe)_6]^{3-}$ and $[Ni(NCSe)_4]^{2-}$. The isoselenocyanate ligand often features nonlinear coordination
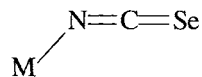
$$\underset{M}{\diagup}N{=\!\!=}C{=\!\!=}Se$$

but in the presence of bulky ligands it tends to become linear $M-\overset{+}{N}{\equiv}C-\overset{-}{Se}$. A bidentate bridging mode is also well established, e.g. $\{Cd-Se-C-N-Cd\}$ and $\{Ag-Se-C-N-Cr\}$. Monodentate organoselenium ligands include

[18] D. DAKTERNIEKS, R. D. GIACOMO, R. W. GABLE and B. F. HOSKINS, *J. Am. Chem. Soc.* **110**, 6762–8 (1988). Later papers are reviewed in S. HUSEBYE and S. V. LINDEMAN, *Main Group Chemistry News*, **3**(4), 8–16 (1996).

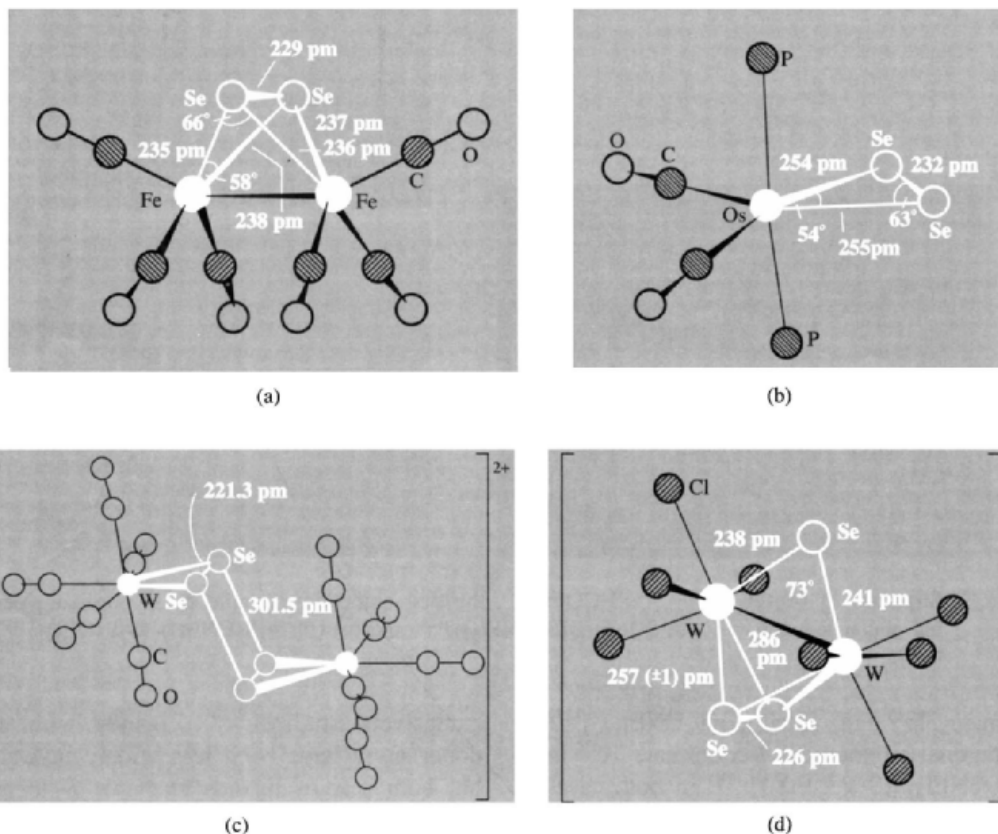[19] S. E. LIVINGSTONE, *Q. Rev.* **19**, 386–425 (1965).

**Figure 16.3** Structures of some $\eta^2$-$Se_2$ complexes. (a) red $[Fe_2(CO)_6(\mu,\eta^2$-$Se_2)]$,[20] (b) reddish-purple $[Os(CO)_2(PPh_3)_2(\eta^2$-$Se_2)]$,[22] (c) the purple-black dication $[W_2(CO)_8(\mu:\eta^2,\eta^2$-$Se_4)]^{2+}$ [23] and (d) brown $[W_2Cl_8(\mu$-$Se)(\mu$-$Se_2)]^{2-}$ [24]

$R_2Se$, $Ar_2Se$, $R_3P{=}Se$ and selenourea $(H_2N)_2C{=}Se$, all of which bond well to heavy metal acceptors. Tellurium appears to be analogous:[3] e.g. $Me_2Te.HgX_2$, $C_4H_8Te.HgCl_2$, $Ph_2Te.HgX_2$, etc.

The structure of complexes containing the $\eta^2$-$Se_2$ ligand have recently been determined and, where appropriate, compared with analogous $\eta^2$-$S_2$, $\eta^2$-$P_2$ and $\eta^2$-$As_2$ complexes (p. 587). Examples are in Fig. 16.3 and the original papers should be consulted for further details.[20−25] Complexes

which feature side-on $\eta^2$-$Te_2$ such as $[Ni(ppp)(\eta^2$-$Te_2)]$ (ppp = $Ph_2PC_2H_4P(Ph)C_2H_4PPh_2$), analogous to the $\eta^2$-$Se_2$ complex in Fig. 16.3b are also

[21] D. J. JONES, T. MAKANI and J. ROZIÈRE, *J. Chem. Soc., Chem. Commun.*, 1275–80 (1986).

[22] D. H. FARRAR, K. R. GRUNDY, N. C. PAYNE, W. R. RO-PER and A. WALKER, *J. Am. Chem. Soc.* **101**, 6577–82 (1979).

[23] M. J. COLLINS, R. J. GILLESPIE, J. W. KOLIS and J. F. SAWYER, *Inorg. Chem.* **25**, 2057–61 (1986).

[24] M. G. B. DREW, G. W. A. FOWLES, E. M. PAGE and D. A. RICE, *J. Am. Chem. Soc.* **101**, 5827–8 (1979). The dark green rhodium complex $[Rh_2(\eta^5$-$C_5Me_5)_2(\mu$-$Se)(\mu$-$Se_2)]$ and the violet-brown osmium analogue $[Os_2(\eta^5$-$C_5Me_5)_2(\mu$-$Se)(\mu$-$Se_2)]$ have a similar structure.[25]

[25] H. BRUNNER, W. MEIER, B. NUBER, J. WACHTER and M. L. ZIEGLER, *Angew. Chem. Int. Edn. Engl.* **25** 907–8 (1986).

[20] C. F. CAMPANA, F. Y.-K. LO, and L. F. DAHL, *Inorg. Chem.* **18**, 3060–4 (1979); see also pp. 3047 and 3054. The mixed-metal cationic complex $[FeW(CO)_8(\mu,\eta^2$-$Se_2)]^{2+}$ has a similar structure.[21]

known,[26] as well as those which feature the $\mu:\eta^2,\eta^2$ bridging mode:[27]

$$L_n Ni \underset{Te}{\overset{Te}{<\ |\ >}} NiL_n$$

The tridentate triangulo ligand $\eta^3$-*cyclo*-$Te_3$ has been characterized in the cationic complex $[W(CO)_4(\eta^3\text{-}Te_3)]^{2+}$ [28] [cf. $\eta^3$-$P_3$ (p. 487), $\eta^3$-$As_3$ (p. 588), etc.], and $\mu_3$- and $\mu_4$-bridging Te atoms have been found in the heptanuclear trimetallic cluster $[\{Fe_2(CO)_6\}(\mu_4\text{-}Te)(\mu_3\text{-}Te)\{Re_3(CO)_{11}\}]$ [29] The core geometry of this latter cluster can be described as a $\{Fe_2Te_2\}$ 'butterfly' with wing-tip Te atoms bridging a bent $Ru_3$ unit.

The compounds of Se, Te and Po should all be treated as potentially toxic. Volatile compounds such as $H_2Se$, $H_2Te$ and organo derivatives are particularly dangerous and maximum permissible limits for air-borne concentrations are $0.1\ mg\ m^{-3}$ (cf. $10\ mg\ m^{-3}$ for HCN). The elements are taken up by the kidneys, spleen and liver, and even in minute concentrations cause headache, nausea and irritation of mucous membrane.

Organoselenium compounds in particular, once ingested, are slowly released over prolonged periods and result in foul-smelling breath and perspiration. The element is also highly toxic towards grazing sheep, cattle and other animals, and, at concentrations above about 5 ppm, causes severe disorders. Despite this, Se was found (in 1957) to play an essential dietary role in animals and also in humans — it is required in the formation of the enzyme glutathione peroxidase which is involved in fat metabolism. It has also been found that the incidence of kwashiorkor (severe protein malnutrition) in children is associated with inadequate uptake of Se, and it may well be involved in protection against certain cancers. The average dietary intake of Se in the USA is said to be $\sim$150 μg daily, usually in meat and sea food. Considerable caution should be taken in handling compounds of Se and Te, but the hazards should also be kept in perspective — no human fatalities directly attributable to either Se or Te poisoning have ever been recorded. The biochemistry and dietary aspects of Se have been reviewed.[30]

Polonium is extremely toxic at all concentrations and is never beneficial. Severe radiation damage of vital organs follows ingestion of even the minutest concentrations and, for the most commonly used isotope, $^{210}Po$, the maximum permissible body burden is $0.03\ \mu Ci$, i.e. 1100 Bq ($\equiv 1100\ s^{-1}$), equivalent to $\sim 7 \times 10^{-12}\ g$ of the element. Concentrations of airborne Po compounds must be kept below $4 \times 10^{-11}\ mg\ m^{-3}$.

## 16.1.6 Polyatomic cations, $M_x^{n+}$

The brightly coloured solutions obtained when sulfur is dissolved in oleums (p. 664) are paralleled by similar behaviour of Se and Te. Indeed, the bright-red solutions of Te in $H_2SO_4$ were noted by M. H. Klaproth in 1798 and the coloured solutions of Se in the same solvent were reported by G. Magnus in 1827. Systematic studies in a range of nonaqueous solvents have since shown that the polycations of Se and Te are less electropositive than their S analogues and can be prepared in a variety of strong acids such as $H_2SO_4$, $H_2S_2O_7$, $HSO_3F$, $SO_2/AsF_5$, $SO_2/SbF_5$ and molten $AlCl_3$.[31,32] Typical reactions for Se are:

[26] M. DI. VAIRA, M. PERUZZINI and P. STOPPIONI, *Angew. Chem. Int. Edn. Engl.* **26**, 916–7 (1987).

[27] M. DI. VAIRA, M. PERUZZINI and P. STOPPIONI, *J. Chem. Soc., Chem. Commun.*, 374–5 (1986).

[28] R. FAGGIANI, R. J. GILLESPIE, C. CAMPANA and J. W. KOLIS, *J. Chem. Soc., Chem. Commun.*, 485–6 (1987).

[29] P. MATHUR, I. J. MAVUNKAL and A. L. RHEINGOLD, *J. Chem. Soc., Chem. Commun.*, 382–4 (1989).
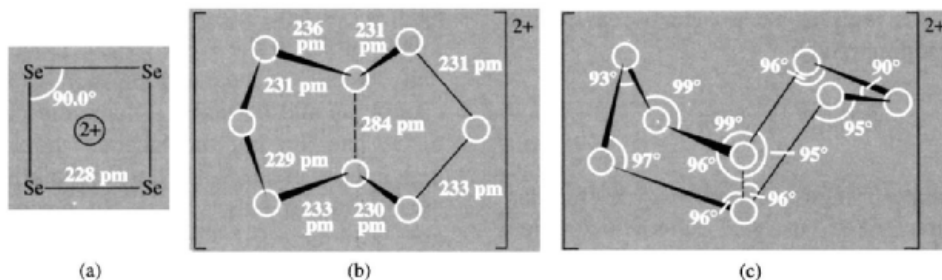
[30] R. J. SHAMBERGER, *Biochemistry of Selenium*, Plenum Press, New York, 1983, 334 pp. C. REILLY, *Selenium in Food and Health*, Blackie, London, 1996, 338 pp.

[31] R. J. GILLESPIE and J. PASSMORE, *Adv. Inorg. Chem. Radiochem.* **17**, 49–87 (1975). M. J. TAYLOR, *Metal–Metal Bonded States in Main Group Elements*, Academic Press, London, 1975, 211 pp. J. D. CORBETT, *Prog. Inorg. Chem.* **21**, 121–58 (1976). T. A. O'DONNELL, *Chem. Soc. Rev.* **16**, 1–43 (1987).

[32] N. BURFORD, J. PASSMORE and J. C. P. SANDERS, Chap. 2, Preparation, Structure and Energetics of the Homopolyatomic Cations of Groups 16 and 17, in J. F. LIEBMAN and A. GREENBURG (eds.), *From Atoms to Polymers: Isoelectronic Analogies*, VCH Publ., Florida, 1989, pp. 53–108. J. PASSMORE, Chap. 19 Homopolyatomic Selenium Cations

**Figure 16.4**    (a) Structure of $[Se_4]^{2+}$; (b) and (c) views of $[Se_8]^{2+}$.
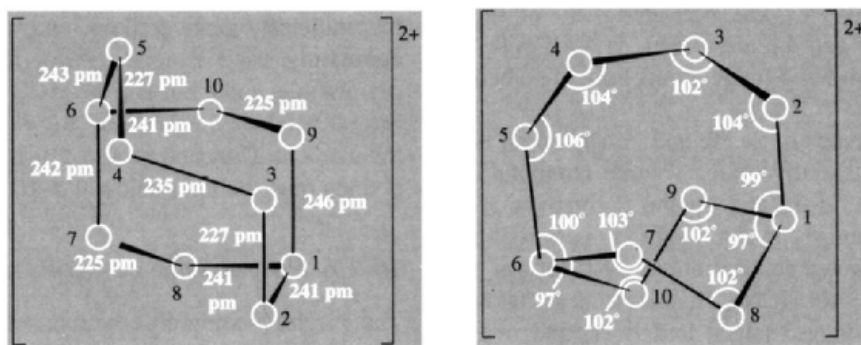


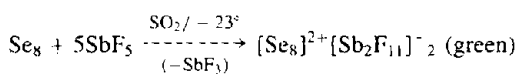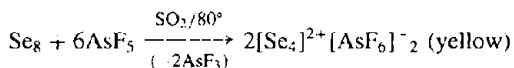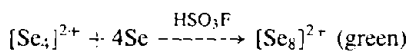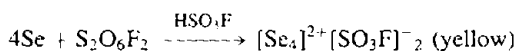**Figure 16.5**    Structure of the $[Se_{10}]^{2+}$ cation in $Se_{10}(SbF_6)_2$ along the *b*- and *c*-axes of the crystal; angles Se(2)-Se(1)-Se(9) and Se(5)-Se(6)-Se(10) are each 101.7°.

$$4Se + S_2O_6F_2 \xrightarrow{HSO_3F} [Se_4]^{2+}[SO_3F]^-{}_2 \text{ (yellow)}$$

$$[Se_4]^{2+} + 4Se \xrightarrow{HSO_3F} [Se_8]^{2+} \text{ (green)}$$

$$Se_8 + 6AsF_5 \xrightarrow[(-2AsF_3)]{SO_2/80°} 2[Se_4]^{2+}[AsF_6]^-{}_2 \text{ (yellow)}$$

$$Se_8 + 5SbF_5 \xrightarrow[(-SbF_3)]{SO_2/-23°} [Se_8]^{2+}[Sb_2F_{11}]^-{}_2 \text{ (green)}$$

$$7\tfrac{1}{2}Se + \tfrac{1}{2}SeCl_4 + 2AlCl_3 \xrightarrow{\text{fuse at 250°}} [Se_8]^{2+}[AlCl_4]^-{}_2$$
$$\text{(green-black)}$$
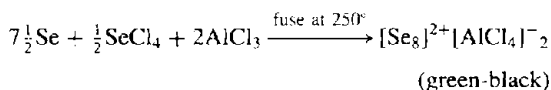
X-ray crystal structure studies on $[Se_4]^{2+}$-$[HS_2O_7]^-{}_2$ show that the cation is square planar (like $S_4^{2+}$, p. 665) as in Fig. 16.4a. The Se–Se distance of 228 pm is significantly less than the value of 234 pm in $Se_8$ and 237 pm in

$Se_\infty$, consistent with some multiple bonding. The structure of $[Se_8]^{2+}$ in the salt $[Se_8]^{2+}[AlCl_4]^-{}_2$ is in Fig. 16.4b and c: it comprises a bicyclo $C_s$ structure with the *endo-exo* configuration with a long trans-annular link of 284 pm. Other Se–Se distances are very similar to those in $Se_8$ itself, but the Se–Se–Se angles are significantly smaller in the cation, being ~96° rather than 106°. More recently[33] the deep-red crystalline compound $Se_{10}(SbF_6)_2$ has been isolated from the reaction of $SbF_5$ with an excess of Se in $SO_2$ under pressure at ~50°. Two views of the bicyclic cation are shown in Fig. 16.5; it features a 6-membered boat-shaped ring linked across the middle of a zigzag chain of 4 further Se atoms. The Se–Se distances vary from 225 to 240 pm and Se–Se–Se angles range from

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and Related Halo-polyselenium Cations, in R. Steudel (ed.), *The Chemistry of Inorganic Ring Systems*, Elsevier, Amsterdam, 1992, pp. 373–407.

[33] R. C. BURNS, W.-L. CHAN, R. J. GILLESPIE, W.-C. LUK, J. F. SAWYER and D. R. SLIM, *Inorg. Chem.* **19**, 1432–9 (1980).

97° to 106°, with 6 angles at the bridgehead atoms Se(1) and Se(6) being significantly smaller than the other 8 in the linking chains. The low-temperature disproportionation of $Se_{10}^{2+}$ into $Se_8^{2+}$ and a second species, probably $Se_{17}^{2+}$, i.e {$Se_8$–$Se$–$Se_8$}$^{2+}$, has been studied by $^{77}Se$ nmr spectroscopy.[34] Heteronuclear species such as $[S_xSe_{4-x}]^{2+}$ have also been identified by nmr techniques and characterized by X-ray structure analysis.[35] Analogous Se/Te heteronuclear cations are described below.

Polyatomic tellurium cations can be prepared by similar routes. The bright-red species $Te_4^{2+}$, like $S_4^{2+}$ and $Se_4^{2+}$, is square planar with the Te–Te distance (266 m) somewhat less than in the element (284 m) (Fig. 16.6a). Oxidation of Te with $AsF_5$ in $AsF_3$ as solvent yields the brown crystalline compound $Te_6(AsF_6)_4.2AsF_3$: X-ray studies reveal the presence of $[Te_6]^{4+}$ which is the first example of a simple trigonal prismatic cluster cation (Fig. 16.6b). The Te–Te distances between the triangular faces (313 pm) are substantially larger than those within the triangle (267 pm).[36] No Te analogue of $S_8^{2+}$ and $Se_8^{2+}$ had been identified until 1997 when the reaction of $ReCl_4$ with Te and $TeCl_4$ at 230° yielded silvery crystals of $[Te_8]^{2+}[ReCl_6]^{2-}$ with Te–Te 272 pm (av), the shortest Te ⋯ Te distance being 315 pm.[36a] Previously (1990), oxidation
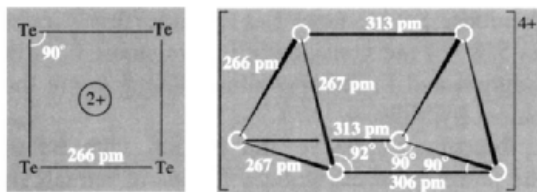
of Te with $WCl_6$ had yielded $[Te_8][WCl_6]_2$ in which the $Te_8^{2+}$ dication was found to have a more pronounced bicyclic structure of $C_2$ symmetry with Te–Te 275.2 pm and the central transannular link being 299.3 pm.[36a]

Mixed Se/Te polatomic cations are also known. For example, when Se and Te are dissolved in 65% oleum at room temperature the resulting orange-brown solutions were shown by $^{125}Te$ and $^{123}Te$ nmr spectroscopy to contain the four species $[Te_nSe_{4-n}]^{2+}$ ($n = 1$–4) and the species $[Se_4]^{2+}$ was also presumably present.[37] Likewise $^{77}Se$ and $^{125}Te$ multinuclear magnetic resonance studies on solutions obtained by oxidizing equimolar mixtures of Se and Te with $AsF_5$ in $SO_2$ reveal not only $[Se_4]^{2+}$, $[Te_4]^{2+}$ and $[Te_6]^{4+}$ but also $[TeSe_3]^{2+}$, *cis-* and *trans-*$[Te_2Se_2]^{2+}$, $[Te_3Se]^{2+}$, $[Te_2Se_4]^{2+}$ and $[Te_3Se_3]^{2+}$.[38] The molecular structures of the sulfur analogue $[Te_3S_3]^{2+}$ and of $[Te_2Se_4]^{2+}$ have also been determined by X-ray diffractometry and found to have a boat-shaped 6-membered heterocyclic structure with a cross-ring bond as shown in Fig. 16.7. As expected, these $M_6^{2+}$ species are more open than the corresponding $Te_6^{4+}$ cluster because of the presence of 2 extra valency-shell electrons (p. 724). Other mixed species that have been characterized include $[Te_2Se_6]^{2+}$ (cube, with diagonally placed Te)[39]
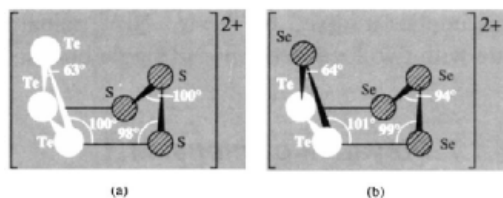


**Figure 16.6** Structure of the cations $[Te_4]^{2+}$ and $[Te_6]^{4+}$.



**Figure 16.7** Structures of the heteroatomic cluster cations (a) $[Te_3S_3]^{2+}$ and (b) $[Te_2Se_4]^{2+}$.

[34] R. C. BURNS, M. J. COLLINS, R. J. GILLESPIE and G. J. SCHROBILGEN, *Inorg. Chem.* **25**, 4465–9 (1986); but see Z. *anorg. allg. Chem.* **623**, 780–4 (1977).

[35] M. J. COLLINS, R. J. GILLESPIE, J. F. SAWYER and G. J. SCHROBILGEN, *Inorg. Chem.* **25**, 2053–7 (1986).

[36] R. C. BURNS, R. J. GILLESPIE, W.-C. LUK and D. R. SLIM, *Inorg. Chem.* **18**, 3086–94 (1979).

[36a] J. BECK and K. MÜLLER-BUSCHBAUM, Z. *anorg. allg. Chem.* **623**, 409–13 (1997) and references therein.

[37] C. R. LASSIGNE and E. J. WELLS, *J. Chem. Soc., Chem. Commun.*, 956–7 (1978).

[38] G. J. SCHROBILGEN, R. C. BURNS and P. GRANGER, *J. Chem. Soc., Chem. Commun.*, 957–60 (1978). P. BOLDRINI, I. D. BROWN, M. J. COLLINS, R. J. GILLESPIE, E. MAHRAJH, D. R. SLIM and J. F. SAWYER, *Inorg. Chem.* **24**, 4302–7 (1985).

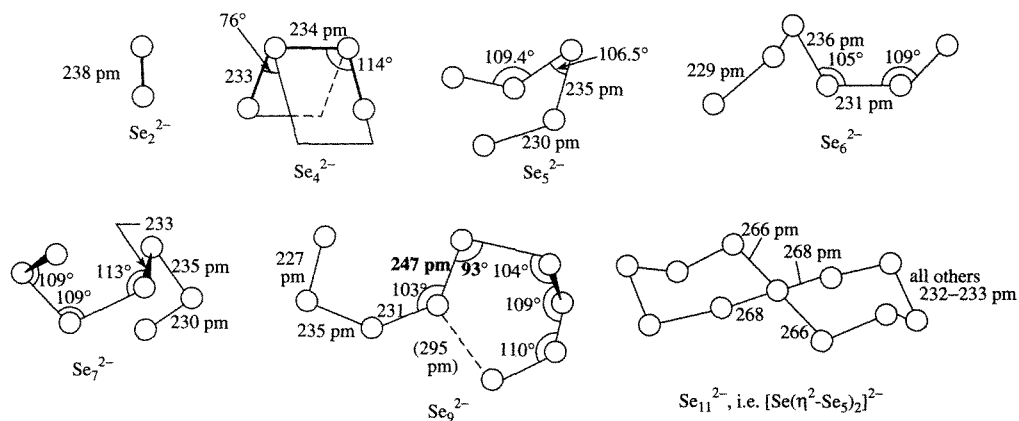[39] M. J. COLLINS and R. J. GILLESPIE, *Inorg. Chem.* **23**, 1975–8 (1984).

**Figure 16.8** Structures of some dianions $Se_x^{2-}$ (see text).

and $[Te_4S_4]^{2+}$ (electron-rich $S_4N_4$ cluster but with coplanar S atoms as in $As_4S_4$).[40]

The mixed *anionic* species $[Tl_2Te_2]^{2-}$ (20 valence electrons) is butterfly-shaped with $Tl_2$ at the "hinge" and 2Te at the "wing tips",[41] in contrast to the 22 valence-electron *cationic* species $Te_4^{2+}$ and $Se_4^{2+}$ which are square planar. The remarkable cationic cluster species $[(NbI_2)_3-O(Te_4)(Te_2)_2]^+$ should also be noted: this was formed serendipitously in low yield as the monoiodide during the high-temperature reaction between $NbOI_3$, Te and $I_2$ and features the bridging groups $(\mu,\eta^2{:}\eta^2\text{-}Te_4)^{2+}$ and two $(\mu,\eta^2\text{-}Te_2)$ in addition to $(\mu_3\text{-}O)^{2-}$ and six terminal $I^-$. This implies a mixed $Nb^{III}$ $Nb^{IV}$ $Nb^{IV}$ oxidation state with two localized Nb–Nb single bonds.[42]

### 16.1.7 Polyatomic anions, $M_x^{2-}$

The synthesis, structural characterization and coordination chemistry of polyselenides, $Se_x^{2-}$, and polytellurides, $Te_x^{2-}$, is a burgeoning field which has sprung into prominence during the past decade. The seminal studies by E. Zintl and his

group during the 1930s showed that such species could be prepared by reduction of the elements with alkali metals in liquid ammonia, but it was the advent of $^{77}Se$ and $^{125}Te$ nmr techniques, and the use of crown and crypt complexes (p. 96) to prepare crystalline derivatives for X-ray structural analysis which provided the firm bases for further advances. The rich reaction chemistry and coordination properties soon followed. Comparisons with polysulfides and polysulfanes (pp. 681–3) are instructive. Thus, little is known about $H_2Se_2$ and $H_2Te_2$, and nothing at all about the higher homologues $H_2Se_x$ and $H_2Te_x$; however, compounds containing the dianions $Se_x^{2-}$ ($x = 2{-}11$) and $Te_x^{2-}$ ($x = 2{-}5, 8 \ldots$) are considerably more stable both in solution and in the crystalline state than are the parent hydrides.

Reaction of $Na_2Se$ and $Na_2Se_2$ with Se in the presence of ethanolic solutions of tetraalkylammonium halides and catalytic amounts of $I_2$ yields dark green or black crystalline polyselenides ($x = 3, 5{-}9$) depending on the conditions used and the particular cation selected.[43] Tetraphenylphosphonium salts and crown ether complexes of alkali or alkaline earth cations in dimethylformamide solution can also be used.[44]

[40] R. FAGGIANI, R. J. GILLESPIE and J. E. VEKRIS, *J. Chem. Soc., Chem. Commun.*, 902–4 (1988).

[41] R. C. BURNS and J. D. CORBETT, *J. Am. Chem. Soc.* **103**, 2627–32 (1981).

[42] W. TREMEL, *J. Chem. Soc., Chem. Commun.*, 126–8 (1992).

[43] F. WELLER, J. ADEL and K. DEHNICKE, *Z. anorg. allg. Chem.* **548**, 125–32 (1987).

[44] D. FENSKE, C. KRAUS and K. DEHNICKE, *Z. anorg. allg. Chem.* **607**, 109–12 (1992). V. MÜLLER, A. AHLE,

Typical structures and dimensions of the resulting polyselenide dianions are shown in Fig. 16.8, though it should be emphasized that torsion angles, interatomic angles and even to some extent interatomic distances may depend on the countercation chosen. Detailed references have been tabulated.[45] The triselenide ion, $Se_3^{2-}$ has been identified as a moderately stable species in solution and in the solid state, but its X-ray structure has not been reported; it is presumably angular like $S_3^{2-}$ and $Te_3^{2-}$. The evolution of the chains up to $Se_7^{2-}$ is clear. The structure of $Se_8^{2-}$ has also been determined in $[Na(crown)]^+{}_2[Se_8]^{2-}(Se_6.Se_7)$ which features a curious packing of the cation and the anion with an equimolar amount of neutral *cyclo*-$Se_n$ comprising variable amounts of $Se_6$ and $Se_7$.[46] The structure of *catena*-$Se_9^{2-}$ has a relatively long central Se—Se bond (247 pm) which forms, at one end, a sharp angle of 93° to the adjacent Se atom; the Se at other end of the bond is approached rather closely by one of the terminal Se atoms (295 pm) to form an incipient 6-membered ring. The process continues in $Se_{11}^{2-}$ which has a centrosymmetric spiro-bicyclic structure involving a central square-planar Se atom common to the two chair-conformation rings. The central bonds are again rather long (266–268 pm) and the structure may be described as a central $Se^{2+}$ chelated by two $\eta^2$-$Se_5^{2-}$ ligands (see below). The structure also has similarities with the anion in $Cs^+{}_4[Se_{16}]^{4-}$,[47] which has a central planar formal $Se^{2+}$ coordinated by one chelating $\eta^2$-$Se_5^{2-}$ ligand (Se—Se 243 pm) and by two monohapto $\eta^1$-$Se_5^{2-}$ ligands (Se—Se 299 pm), i.e. $[Se(\eta^2$-$Se_5)(\eta^1$-$Se_5)_2]^{2-}$.

Several of the *catena*-$Se_x^{2-}$ anions have proved to be effective chelating ligands to both main-group and transition metals. Synthesis of the complexes is usually via direct reaction with the preformed anion or by synthesis of the anion in the presence of the appropriate metal centre. Examples are $[Sn(\eta^2$-$Se_4)_3]^{2-}$,[48] $[M(\eta^2$-$Se_4)_2]^{2-}$ (M = Zn, Cd, Hg, Ni, $Pb^{II}$),[49] $[Mo^{IV}(\eta^5$-$C_5H_5)(\eta^2$-$Se_4)_2]^{-}$[50] and $[M_3(Se_4)_6]^{3-}$, i.e. $[\{M(Se_4)_3\}M\{(Se_4)_3M\}]^{3-}$ (M = Cr,[51] Co[52]), in which the two terminal $M^{III}$ atoms have approximately *tris*-tetraselenide chelate coordination whilst the central $M^{III}$ atom (also approximately octahedral) has $(\mu$-$Se)_6$ coordination, achieved by sharing one 'terminal' Se atom from each of the six $Se_4$ groups. The complex $[Ti(\eta^5$-$C_5H_5)_2(\eta^2$-$Se_5)]$ reacts with $SCl_2$, $S_2Cl_2$ and $SeCl_2$ to form, respectively, $Se_5S$, $Se_5S_2$ and $Se_7$.[53] Heterocyclic chelating ligands are also known, e.g. in $[PtCl(PMe_2Ph)(\eta^2$-$Se_3N)]$.[54] Note also the extraordinary 1900 pm long hexameric anion, $[Ga_6Se_{14}]^{10-}$, which is composed of a linear array of edge-sharing $\{GaSe_4\}$ units, i.e. $[Se_2\{Ga(\mu$-$Se)_2\}_5GaSe_2]^{10-}$.[55]

Polytellurides, $Te_x^{2-}$, are less straightforward and often form complex units coordinated to metal centres.[56] The isolated ions $Te_2^{2-}$ and

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[48] S.-P. HUANG, S. DHINGRA and M. G. KANATZIDIS, *Polyhedron* **9**, 1389–95 (1990).

[49] R. M. H. BANDA, J. CUSICK, M. L. SCUDDER, D. C. CRAIG and I. G. DANCE, *Polyhedron* **8**, 1995–8 (1989). S. MAGULL, K. DEHNICKE and D. FENSKE, *Z. anorg. allg. Chem.* **608**, 17–22 (1992).

[50] R. M. H. BANDA, J. CUSICK, M. L. SCUDDER, D. C. CRAIG and I. G. DANCE, *Polyhedron* **8**, 1999–2001 (1989). See also J. CUSICK, M. L. SCUDDER, D. C. CRAIG and I. G. DANCE, *Polyhedron* **8**, 1139–41 (1989) for the more complex structures of tetranuclear Cu and Ag polyselenides.

[51] W. A. FLOMER, S. C. O'NEAL, W. T. PENNINGTON, D. JETER, A. W. CORDES and J. W. KOLIS, *Angew. Chem. Int. Edn. Engl.* **27**, 1702–3 (1988).

[52] J. CUSICK, M. L. SCUDDER, D. C. CRAIG and I. G. DANCE, *Aust. J. Chem.* **43**, 209–11 (1990).

[53] R. STEUDEL, M. PAPAVASSILIOU, E.-M. STRAUSS and R. LAITINEN, *Angew. Chem. Int. Edn. Engl.* **25**, 99–101 (1986).

[54] P. F. KELLY, A. M. Z. SLAWIN, D. J. WILLIAMS and J. D. WOOLLINS, *J. Chem. Soc., Chem. Commun.*, 408–9 (1989).

[55] E. NIECKE, K. SCHWICHTENHÖVEL, H. G. SCHÄFER and B. KREBS, *Angew. Chem. Int. Edn. Engl.* **20**, 962–3 (1981).

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G. FRENZEN, B. NEUMÜLLER and K. DEHNICKE, *Z. anorg. allg. Chem.* **619**, 1247–56 (1993). V. MÜLLER, C. GREBE, U. MÜLLER and K. DEHNICKE, *Z. anorg. allg. Chem.* **619**, 416–20 (1993).

[45] J. CUSICK and I. DANCE, *Polyhedron* **10**, 2629–40 (1991).

[46] R. STAFFEL, U. MÜLLER, A. AHLE and K. DEHNICKE, *Z. Naturforsch.* **46b**, 1287–92 (1992).

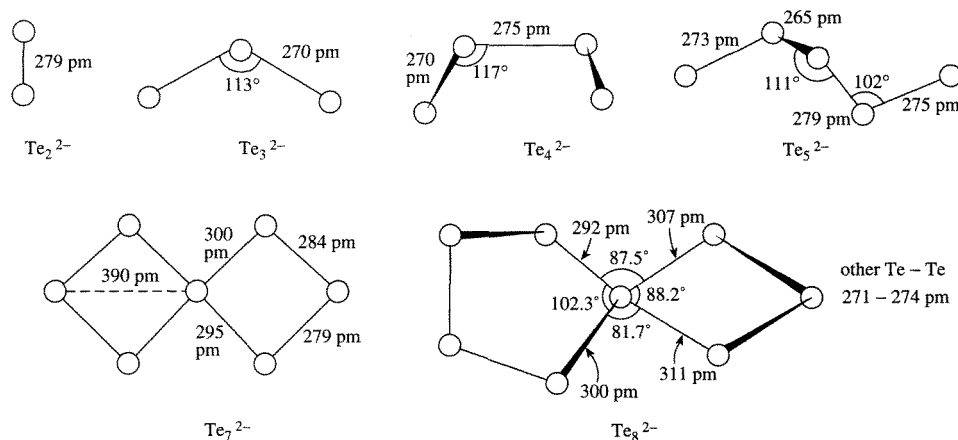[47] W. S. SHELDRICK and H. G. BRAUNBECK, *Z. Naturforsch.*, **44b** 1397–401 (1989).

**Figure 16.9** Structures of some dianions $Te_x^{2-}$ (see text).

$Te_3^{2-}$ are found in $K_2Te_2$, $Rb_2Te_2$[57] and $[K(crypt)]_2Te_3$[58] — see Fig. 16.9. Likewise, $Te_4^{2-}$ has been characterized in salts of crown ether complexes of Ca, Sr and Ba, and $Te_5^{2-}$ as its salt with $[Ph_3PNPPh_3]^+$[59] (Fig. 16.9). The bicyclic polytellurides $Te_7^{2-}$[60] and $Te_8^{2-}$[61] are also known (Fig. 16.9). However, simple stoichiometry often conceals structural complexity as in the many alkali metal tellurides $MTe_x$ ($x = 1, 1.5, 2.5, 3, 4$).[56,62]

There is also a bewildering variety of structural motifs in polytelluride–ligand complexes as the brief selection in Fig. 16.10 indicates; the original papers should be consulted for preparative routes and other details. Thus, dissolution of the alloy $K_2Hg_2Te_3$ in ethylenediamine, followed by treatment with a methanolic solution of $[NBu_4^n]Br$, yields the dark brown compound $[NBu_4^n]_4[Hg_4Te_{12}]$;[63] this features the remarkable anion $[Hg_4Te_{12}]^{4-}$ in which the four Hg atoms, which are coplanar, are coordinated in distorted tetrahedral fashion to an array of two $Te^{2-}$, two $Te_2^{2-}$ and two $Te_3^{2-}$ ligands (Fig. 16.10). By contrast, use of $[PPh_4]^+$ as the counter-cation yields the unbranched, approximately planar, polymeric anion $[\{Hg_2Te_5\}^{2-}]_\infty$ (Fig. 16.10) which contains $\{Hg_2Te_3\}$ heterocycles joined by bridging $Te_2^{2-}$ units.[63] $Cu^I$ and $Ag^I$ form discrete polytelluride complexes in $[PPh_4]_2[M_2Te_{12}]$[64] (Fig. 16.10) containing two chelating and one bridging $Te_4^{2-}$ groups. A similar chelating mode occurs in $[Pd(\eta^2-Te_4)_2]^{2-}$.[65] Discrete $[HgTe_7]^{2-}$ ions occur in the $[K(crown)_2]^+$ salt whereas the corresponding Zn derivative has a polymeric structure[66] (Fig. 16.10). The soluble cluster anion $NbTe_{10}^{3-}$ is also notable; its structure has been determined in the black, crystalline tetraphenylphosphonium salt.[67] Cubane-like clusters occur

[57] P. BÖTTCHER, J. GETZSCHMANN and R. KELLER, *Z. anorg. allg. Chem.* **619**, 476–88 (1993).

[58] A. CISAR and J. D. CORBETT, *Inorg. Chem.* **16**, 632–5 (1977).

[59] D. FENSKE, G. BAUM, H. WOLKERS, B. SCHREINER, F. WELLER and K. DEHNICKE, *Z. anorg. allg. Chem.* **619**, 489–99 (1993).

[60] B. HARBRECHT and A. SELMER, *Z. anorg. allg. Chem.* **620**, 1861–6 (1994).

[61] B. SCHREINER, K. DEHNICKE, K. MACZEK and D. FENSKE, *Z. anorg. allg. Chem.* **619**, 1414–8 (1993).

[62] J. BERNSTEIN and R. HOFFMANN, *Inorg. Chem.* **24**, 4100–8 (1985).

[63] R. C. HAUSHALTER, *Angew. Chem. Int. Edn. Engl.* **24**, 433–5 (1985).

[64] D. FENSKE, B. SCHREINER and K. DEHNICKE, *Z. anorg. allg. Chem.* **619**, 253–60 (1993).

[65] R. D. ADAMS, T. A. WOLFE, B. W. EICHHORN and R. C. HAUSHALTER, *Polyhedron* **8**, 701–3 (1989).

[66] U. MÜLLER, C. GREBE, B. NEUMÜLLER, B. SCHREINER and K. DEHNICKE, *Z. anorg. allg. Chem.* **619**, 500–6 (1993).

[67] W. A. FLOMER and J. W. KOLIS, *J. Am. Chem. Soc.* **110**, 3682–3 (1988).
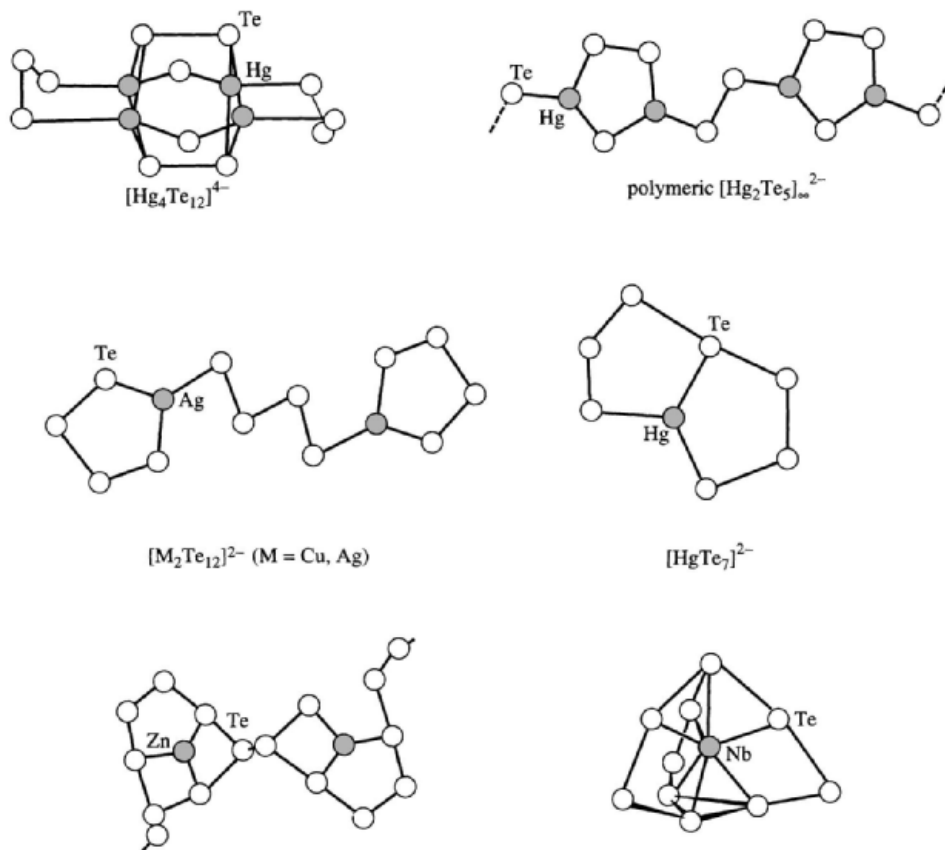
**Figure 16.10**    Structures of some metal-polytelluride complexes.

in $[NEt_4]_3[Fe_4(\mu_3\text{-}Te)_4(TePh)_4].2MeCN^{(68)}$ and, perhaps surprisingly, in $NaTe_3$ which has cubane-like interlinked clusters of $Te_{12}^{6-}$.[69] The tri-nuclear anion $[Cr_3Te_{24}]^{3-}$ has the same structure as its Se analogue (p. 763).[51] Mention could also be made of the planar ion $[TeS_3]^{2-}$ and the spiro-bicyclic $[Te(\eta^2\text{-}S_5)_2]^{2-}$ 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