Table 16.7 Some physical properties of selenium oxohalides

Property	$SeOF_2$	$SeOCl_2$	$SeOBr_2$	SeO_2F_2	$(SeOF_4)_2$	F_5SeOF	$F_5SeOOSF_5$
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, $SeOF_2$ and $SeOCl_2$ are colourless, fuming, volatile liquids, whereas $SeOBr_2$ is a rather less-stable orange solid which decomposes in air above 50° (Table 16.7). The compounds can be conveniently made by reacting SeO_2 with the appropriate tetrahalide and their molecular structure is probably pyramidal (like SOX_2, p. 694). $SeOF_2$ is an aggressive reagent which attacks glass, reacts violently with red phosphorus and with powdered SiO_2 and slowly with Si. In the solid state, X-ray studies have revealed that the pyramidal $SeOF_2$ units are linked by O and F bridges into layers thereby building a distorted octahedral environment around each Se with 3 close contacts (to O and 2F) and 3 (longer) bridging contacts grouped around the lone-pair to neighbouring units.[109] This contrasts with the discrete molecular structure of SOF_2 and affords yet another example of the influence of preferred coordination number on the structure and physical properties of isovalent compounds, e.g. molecular BF_3 and 6-coordinate AlF_3, molecular GeF_4 and the 6-coordinate layer lattice of SnF_4 and, to a less extent, molecular AsF_3 and F-bridged SbF_3. (See also the Group 14 dioxides, etc.)

$SeOCl_2$ (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: $2SeOCl_2 \rightleftharpoons SeOCl^+ + SeOCl_3^-$.

Oxohalides of Se^{VI} are known only for fluorine (Table 16.7). SeO_2F_2 is a readily hydrolysable colourless gas which can be made by fluorinating SeO_3 with SeF_4 (or KBF_4 at 70°) or by reacting $BaSeO_4$ with HSO_3F under reflux at 50°. Its vibrational spectra imply a tetrahedral structure with C_{2v} symmetry as expected. By contrast, $SeOF_4$ is a dimer $[F_4Se(\mu\text{-}O)_2SeF_4]$ in which each Se achieves octahedral coordination via the 2 bridging O atoms: the planar central Se_2O_2 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 SeO_2 with a mixture of F_2/N_2: at 80° the main product is the "hypofluorite" F_5SeOF whereas at 120° the peroxide $F_5SeOOSF_5$ predominates. The compounds (Table 16.7) can be purified by

D. S. URCH, *J. Chem. Soc.* 5775−81 (1964); N. N. GREENWOOD and B. P. STRAUGHAN, *J. Chem. Soc.* (A) 962−4 (1966); T. C. GIBB, R. GREATREX, N. N. GREENWOOD and A. C. SARMA, *J. Chem. Soc.* (A) 212−17 (1970). J. D. DONALDSON, S. D. ROSS, J. SILVER and P. WATKISS, *J. Chem. Soc., Dalton Trans.*, 1980−3 (1975), and references therein. There is, however, some very recent X-ray crystallographic evidence that the anion in $[Bu^tNH_3]_2^+[TeBr_6]^{2-}$ is trigonally distorted, with 3 long bonds of 276 pm (av.) and 3 shorter bonds of 261 pm, although the corresponding $TeCl_6^{2-}$ salt had regular octahedral O_h symmetry: see L.-J. BAKER, C. E. F. RICKARD and M. J. TAYLOR, *Polyhedron* **14**, 401−5 (1995).

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

[110] H. OBERHAMMER and K. SEPPELT, *Inorg. Chem.* **18**, 2226−9 (1979).

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

$$Xe(OSeF_5)_2 \xrightarrow{130°} Xe + \tfrac{1}{2}O_2 + F_5SeOSeF_5$$

The corresponding tellurium analogue, F_5Te-$TeOF_5$, is made by fluorinating TeO_2 in a copper vessel at $60°$ using a stream of F_2/N_2 (1:10); it is a colourless, mobile, unreactive liquid, mp $-36.6°$ bp $59.8°$.[76,77] The Se–O–Se angle in $F_5SeOSeF_5$ is $142.4°$ ($\pm1.9°$) as in the sulfur analogue, and the Te–O–Te angle is very similar ($145.5 \pm 2.1°$). The fluorination of Te in the presence of oxygen yields (in addition to $Te_2F_{10}O$, p. 767) the dense colourless liquids $Te_3^{VI}O_2F_{14}$ and $Te_6^{VI}O_5F_{26}$. More purposeful synthetic routes have also been devised, leading to the isolation and structural characterization of the 6-coordinate Te^{VI} oxofluorides *cis*- and *trans*-$F_4Te(OTeF_5)_2$, *cis*- and *trans*-$F_2Te(OTeF_5)_4$, $FTe(OTeF_5)_5$ and even $Te(OTeF_5)_6$.[112] Similarly, thermolysis of $B(OTeF_5)_3$ at $600°$ in a flow system yields the oxygen-bridged dimer $Te_2O_2F_8$ analogous to $Se_2O_2F_8$ above. $Te_2O_2F_8$ is a colourless liquid with a garlic-like smell, mp $28°$, bp $77.5°$. The planar central Te_2O_2 ring has Te–O $192\,pm$ and angle Te–O–Te $99.5°$, and again the equatorial Te–F distances ($180\,pm$) are shorter than the axial ones ($185\,pm$).[110]

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

$$IF_5 + B(OTeF_5)_3 \longrightarrow FI(OTeF_5)_4$$

$$XeF_4 + B(OTeF_5)_3 \longrightarrow Xe(OTeF_5)_4$$

(see also p. 899)

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

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

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

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

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

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

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

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

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

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

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

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

Oxides

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

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

16.2.5 Oxides

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

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

---

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

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

combination of the elements. SeO_2 is a white solid which melts in a sealed tube to a yellow liquid at 340° (sublimes at 315°/760 mmHg). It is very soluble in water to give selenous acid H_2SeO_3 from which it can be recovered by dehydration. It is also very soluble (as a trimer) in $SeOCl_2$ and in H_2SO_4 in which it behaves as a weak base. SeO_2 is thermodynamically less stable than either SO_2 or TeO_2 and is readily reduced to the elements by NH_3, N_2H_4 or aqueous SO_2 (but not gaseous SO_2). It also finds use as an oxidizing agent in organic chemistry. In the solid state SeO_2 has a polymeric structure of corner-linked flattened {SeO_3} pyramids each carrying a pendant terminal O atom:

TeO_2 is dimorphic: the yellow, orthorhombic mineral tellurite (β-TeO_2) has a layer structure in which pseudo-trigonal bipyramidal {TeO_4} groups form edge-sharing pairs (Fig. 16.16a) which then further aggregate into layers (Fig. 16.16b) by sharing the remaining vertices. By contrast, synthetic α-TeO_2 ("paratellurite")

(a)   (b)   (c)

Figure 16.16 Structural units in crystalline TeO_2: (a) pair of edge-sharing pseudo-trigonal bipyramidal {TeO_4} groups in tellurite (β-TeO_2) which aggregate into layers as shown in (b) by sharing the remaining vertices with neighbouring pairs, and (c) the {TeO_4} unit in paratellurite (α-TeO_2).

forms colourless tetragonal crystals in which very similar {TeO$_4$} units (Fig. 16.16c) share all vertices (angle Te–O–Te 140°) to form a rutile-like (p. 961) three-dimensional structure. TeO$_2$ melts to a red liquid at 733° and is much less volatile than SeO$_2$. It can be prepared by the action of O$_2$ on Te, by dehydrating H$_2$TeO$_3$ or by thermal decomposition of the basic nitrate above 400°. TeO$_2$ is not very soluble in water; it is amphoteric and shows a minimum in solubility (at pH ~ 4.0). It is, however, very soluble in SeOCl$_2$.

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

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

Compound	SO$_2$	SeO$_2$
Coordination number	2	3
Structure	molecule	chain polymers

Compound	TeO$_2$	PoO$_2$
Coordination number	4	8
Structure	layer or 3D	3D "fluorite"

The difficulty of oxidizing Se to the +6 state has already been mentioned (p. 755). Indeed, unlike SO$_3$ and TeO$_3$, SeO$_3$ is thermodynamically unstable with respect to the dioxide:

$$\text{SeO}_3 \longrightarrow \text{SeO}_2 + \tfrac{1}{2}\text{O}_2; \quad \Delta H° = -46 \text{ kJ mol}^{-1}$$

Some comparative figures for the standard heats of formation $-\Delta H_f°$ are in Table 16.8. Accordingly, SeO$_3$ can not be made by direct oxidation of Se or SeO$_2$ and is even hard to make by the dehydration of H$_2$SeO$_4$ with P$_2$O$_5$; a better

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

SO$_2$	297	SeO$_2$	230	TeO$_2$	325
SO$_3$	432	SeO$_3$	184	TeO$_3$	348

route is to treat anhydrous K$_2$SeO$_4$ with SO$_3$ under reflux, followed by vacuum sublimation at 120°. SeO$_3$ is a white, hygroscopic solid which melts at 118°, sublimes readily above 100° (40 mmHg) and decomposes above 165°. The crystal structure is built up from cyclic tetramers, Se$_4$O$_{12}$, which have a configuration very similar to that of (PNCl$_2$)$_4$ (p. 538). In the vapour phase, however, there is some dissociation into the monomer. In the molten state SeO$_3$ is probably polymeric like the isoelectronic polymetaphosphate ions (p. 528).

TeO$_3$ exists in two modifications. The yellow-orange α-form and the more stable, less reactive, grey β-form. The α-TeO$_3$ is made by dehydrating Te(OH)$_6$ (p. 782) at 300–360°; the β-TeO$_3$ is made by heating α-TeO$_3$ or Te(OH)$_6$ in a sealed tube in the presence of H$_2$SO$_4$ and O$_2$ for 12 h at 350°. α-TeO$_3$ has a structure like that of FeF$_3$, in which TeO$_6$ octahedra share all vertices to give a 3D lattice. It is unattacked by water, but is a powerful oxidizing agent when heated with a variety of metals or non-metals. It is also soluble in hot concentrated alkalis to form tellurates (p. 782). The β-form is even less reactive but can be cleaved with fused KOH.

PoO$_3$ may have been detected on a tracer scale but has not been characterized with weighable amounts of the element.

16.2.6 Hydroxides and oxoacids

The rich oxoacid chemistry of sulfur (pp. 705–21) is not paralleled by the heavier elements of the group. The redox relationships have already been summarized (p. 755). Apart from the dark-brown hydrated monoxide "Po(OH)$_2$", which precipitates when alkali is added to a freshly prepared solution of Po(II), only compounds in the +4 and +6 oxidation states are known.

Selenous acid, O=Se(OH)$_2$, i.e. H$_2$SeO$_3$, and tellurous acid, H$_2$TeO$_3$, are white solids which can readily be dehydrated to the dioxide (e.g. in a stream of dry air). H$_2$SeO$_3$ is best prepared by slow crystallization of an aqueous solution of SeO$_2$ or by oxidation of powdered Se with dilute nitric acid:

$$3Se + 4HNO_3 + H_2O \longrightarrow 3H_2SeO_3 + 4NO$$

The less-stable H$_2$TeO$_3$ is obtained by hydrolysis of a tetrahalide or acidification of a cooled aqueous solution of a telluride. Crystalline H$_2$SeO$_3$ is built up of pyramidal SeO$_3$ groups (Se–O 174 pm) which are hydrogen-bonded to give an orthorhombic layer lattice. The detailed structure of H$_2$TeO$_3$ is unknown. Both acids form acid salts MHSeO$_3$ and MHTeO$_3$ by reaction of the appropriate aqueous alkali. The neutral salts M$_2$SeO$_3$ and M$_2$TeO$_3$ can be obtained similarly or by heating the metal oxide with the appropriate dioxide. Dissociation constants have not been precisely determined but approximate values are:

H$_2$SeO$_3$: $K_1 \sim 3.5 \times 10^{-3}$ $K_2 \sim 5 \times 10^{-8}$
H$_2$TeO$_3$: $K_1 \sim 3 \times 10^{-3}$ $K_2 \sim 2 \times 10^{-8}$

Alkali diselenites M$_2^I$Se$_2$O$_5$ are also known and appear (on the basis of vibrational spectroscopy) to contain the ion [O$_2$Se–O–SeO$_2$]$^{2-}$, with C_{2v} symmetry and a nonlinear Se–O–Se bridge (cf. disulfite O$_3$S–SO$_2{}^{2-}$, p. 720). Selenous acid, in contrast to H$_2$TeO$_3$, can readily be oxidized to H$_2$SeO$_4$ by ozone in strongly acid solution; it is reduced to elementary selenium by H$_2$S, SO$_2$ or aqueous iodide solution.

Hydrated polonium dioxide, PoO(OH)$_2$, is obtained as a pale-yellow flocculent precipitate by addition of dilute aqueous alkali to a solution containing Po(IV). It is appreciably acidic, e.g.:

$$PoO(OH)_2 + 2KOH \underset{22°}{\rightleftharpoons} K_2PoO_3 + 2H_2O;$$

$$K_a = \frac{[PoO_3{}^{2-}]}{[OH^-]^2} = 8.2 \times 10^{-5}$$

In the +6 oxidation state the oxoacids of Se and Te show little resemblance to each other. H$_2$SeO$_4$ resembles H$_2$SO$_4$ (p. 710) whereas orthotelluric acid Te(OH)$_6$ and polymetatelluric acid (H$_2$TeO$_4$)$_n$ are quite different.

Anhydrous H$_2$SeO$_4$ is a viscous liquid which crystallizes to a white deliquescent solid (mp 62°). It loses water on being heated and combines readily with SeO$_3$ to give "pyroselenic acid", H$_2$Se$_2$O$_7$ (mp 19°), and triselenic acid, H$_4$Se$_3$O$_{11}$ (mp 25°). It also resembles H$_2$SO$_4$ in forming several hydrates: H$_2$SeO$_4$.H$_2$O (mp 26°) and H$_2$SeO$_4$.4H$_2$O (52°). Crystalline H$_2$SeO$_4$ (d 2.961 g cm^{-3}) comprises tetrahedral SeO$_4$ groups strongly H-bonded into layers through all 4 O atoms (Se–O 161 pm, O–H$\cdots$O 261–268 pm). H$_2$SeO$_4$ can be prepared by several routes:

(i) Oxidation of H$_2$SeO$_3$ with H$_2$O$_2$, KMnO$_4$ or HClO$_3$, which can be formally represented by the equations:

$$H_2SeO_3 + H_2O_2 \longrightarrow H_2SeO_4 + H_2O$$

$$8H_2SeO_3 + 2KMnO_4 \longrightarrow 5H_2SeO_4$$
$$+ K_2SeO_3 + 2MnSeO_3 + 3H_2O$$

$$5H_2SeO_3 + 2HClO_3 \longrightarrow 5H_2SeO_4$$
$$+ Cl_2 + H_2O$$

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

$$Se + 3Cl_2 + 4H_2O \longrightarrow H_2SeO_4 + 6HCl$$

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

$$Ag_2SeO_3 + Br_2 + H_2O \longrightarrow$$
$$H_2SeO_4 + 2AgBr$$

The acid dissociation constants of H$_2$SeO$_4$ are close to those of H$_2$SO$_4$, e.g. K_2 (H$_2$SeO$_4$)

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

$$2Au + 6H_2SeO_4 \longrightarrow Au_2(SeO_4)_3$$
$$+ 3H_2SeO_3 + 3H_2O$$

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

By contrast, the two main forms of telluric acid do not resemble H_2SO_4 and H_2SeO_4 and tellurates are not isomorphous with sulfates and selenates. Orthotelluric acid is a white solid, mp 136°, whose crystal structure is built up of regular octahedral molecules, $Te(OH)_6$. This structure, which persists in solution (Raman spectrum), is also reflected in its chemistry; e.g. breaks occur in the neutralization curve at points corresponding to NaH_5TeO_6, $Na_2H_4TeO_6$, $Na_4H_2TeO_6$ and Na_6TeO_6. Similar salts include Ag_6TeO_6 and Hg_3TeO_6. Moreover diazomethane converts it to the hexamethyl ester $Te(OMe)_6$. In this respect Te resembles its horizontal neighbours in the periodic table Sn, Sb and I which form the isoelectronic species $[Sn(OH)_6]^{2-}$, $[Sb(OH)_6]^-$ and $IO(OH)_5$. Orthotelluric acid can be prepared by oxidation of powdered Te with chloric acid solution or oxidation of TeO_2 with permanganate in nitric acid:

$$5Te + 6HClO_3 + 12H_2O \longrightarrow 5H_6TeO_6 + 3Cl_2$$
$$5TeO_2 + 2KMnO_4 + 6HNO_3 + 12H_2O \longrightarrow$$
$$5H_6TeO_6 + 2KNO_3 + 2Mn(NO_3)_2$$

Alternatively, Te or TeO_2 can be oxidized by CrO_3/HNO_3 or by 30% H_2O_2 under reflux. Acidification of a tellurate with an appropriate precipitating acid offers a further convenient route:

$$BaTeO_4 + H_2SO_4 + 2H_2O \longrightarrow BaSO_4\downarrow + H_6TeO_6$$
$$Ag_2TeO_4 + 2HCl + 2H_2O \longrightarrow 2AgCl\downarrow + H_6TeO_6$$

Crystallization from aqueous solutions below 10° gives the tetrahydrate $H_6TeO_6.4H_2O$. The anhydrous acid is stable in air at 100° but above 120° gradually loses water to give polymetatelluric acid and allotelluric acid (see below). Unlike H_2SO_4 and H_2SeO_4, H_6TeO_6 is a weak acid, approximate values of its successive dissociation constants being $K_1 \sim 2 \times 10^{-8}$, $K_2 \sim 10^{-11}$, $K_3 \sim 3 \times 10^{-15}$. It is a fairly strong oxidant, being reduced to the element by SO_2 and to H_2TeO_3 in hot HCl:

$$H_6TeO_6 + 3SO_2 \longrightarrow Te + 3H_2SO_4$$
$$H_6TeO_6 + 2HCl \longrightarrow H_2TeO_3 + 3H_2O + Cl_2$$

Polymetatelluric acid $(H_2TeO_4)_{\sim 10}$ is a white, amorphous hygroscopic powder formed by incomplete dehydration of H_6TeO_6 in air at 160°. Alternatively, in aqueous solution the equilibrium $nH_6TeO_6 \rightleftharpoons (H_2TeO_4)_n + 2nH_2O$ can be shifted to the right by increasing the temperature; rapid cooling then precipitates the sparingly soluble polymetatelluric acid. The structure is unknown but appears to contain 6-coordinate Te. Allotelluric acid "$(H_2TeO_4)_3(H_2O)_4$" is an acid syrup obtained by heating $Te(OH)_6$ in a sealed tube at 305°: the compound has not been obtained pure but tends to revert to H_6TeO_6 at room temperature or to $(H_2TeO_4)_n$ when heated in air; indeed, it may well be a mixture of these two substances.

Tellurates are prepared by fusing a tellurite with a corresponding nitrate, by oxidizing a tellurite with chlorine, by or neutralizing telluric acid with a hydroxide.[123] An interesting variant is to heat intimate mixtures of TeO_3 with metal oxides. For example, with Rb_2O at 680° for several weeks, colourless crystals having the unusual stoichiometry $Rb_6Te_2^{VI}O_9$ were formed which contained both tetrahedral TeO_4^{2-} and trigonal bipyramidal TeO_5^{4-} groups, i.e. $Rb_6[TeO_5][TeO_4]$.[124]

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

123 Ref. 11, pp. 94–7.
124 T. WISSER and R. HOPPE, Z. anorg. allg. Chem. **584**, 105–13 (1990).

Figure 16.17   Structures and conformations of unbranched chain anions in (a) $Ba[Se(S_2O_3)_2].2H_2O$, (b) $Ba[Te(S_2O_3)_2].2H_2O$, and (c) $(NH_4)_2[Te(S_2O_3)_2]$.

described. Examples are peroxoselenous acid $HOSeO(OOH)$ (stable at $-10°$) and potassium peroxo-orthotellurate $K_2H_4TeO_7$ which also loses oxygen at room temperature. Isomeric selenosulfates, $M_2^ISO_3Se$, and thioselenates, $M_2^ISeO_3S$, are known and can be made by the obvious routes of $[SO_3^{2-}(aq) + Se]$ and $[SeO_3^{2-}(aq) + S]$. Likewise, colourless or yellow-green crystalline selenopolythionates $M_2Se_xS_yO_6$ ($x = 1, 2; y = 2, 4$) and orange-yellow telluropentathionates $M_2^ITeS_4O_6$ are known. X-ray structure analysis reveals unbranched chains with various conformations as found for the polythionates themselves (p. 718).[125] Typical examples are in Fig. 16.17. It will be seen that these compounds contain Se and Te bonded to S rather than O and they therefore form a natural link with the Group 16 sulfides to be described in the next section.

16.2.7 Other inorganic compounds

The red compound Se_4S_4, obtained by fusing equimolar amounts of the elements, is a covalent molecular species which can be crystallized from benzene. Similar procedures yield Se_2S_6, SeS_7 and TeS_7, all of which are structurally related to S_8 (p. 654; see also p. 763).

PoS forms as a black precipitate when H_2S is added to acidic solutions of polonium compounds. Its solubility product is $\sim 5 \times 10^{-29}$. The

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

The chemistry of compounds containing Se–N and Te–N bonds has been very activity developed during the past decade and many new and unusual species are emerging.[126,127] Se_4N_4 is an orange, shock sensitive crystalline compound which decomposes violently at $160°$. It resembles its sulfur analogue (p. 722) in being thermochroic (yellow-orange at $-195°$, red at $+100°$) and in having the same D_{2d} molecular structure. Se_4N_4 can be made by reacting anhydrous NH_3 with $SeBr_4$ (or with SeO_2 at $70°$ under pressure). A new red-brown crystalline modification, β-Se_4N_4, which has a very similar cluster structure but differs in the packing arrangement, has recently been prepared by reacting SeO_2 with the phosphane imine, $Me_3SiNPMe_3$.[128] Tellurium nitride can be prepared similarly ($TeBr_4 + NH_3$); it is a lemon-yellow, violently explosive compound with a formula that might be Te_3N_4 rather than Te_4N_4; its structure is unknown.

Se_4N_4 reacts with $[PtCl_2(PMe_2Ph)_2]$ in liquid ammonia (50 atm.) to give a quantitative yield of $[Pt(\eta^2\text{-}Se_2N_2)(PMe_2Ph)_2]$ which features a

[125] A. F. WELLS, *Structural Inorganic Chemistry*, 5th edn., pp. 726–35, Oxford University Press, Oxford, 1984. See also *J. Chem. Soc., Dalton Trans.*, 1528–32 (1978) ($Pb_2Te_3O_8$). *Inorg. Chem.* **19**, 1040–3, 1044–8, 1063–4 (1980) ($SeS_3O_6^{2-}$, $Se_2S_2O_6^{2-}$, $SeS_2O_6^{2-}$).

[126] M. BJÖRGVINSSON and H. W. ROESKY, *Polyhedron* **10**, 2353–70 (1991).
[127] P. F. KELLY   A. M. Z. SLAWIN,   D. J. WILLIAMS   and J. D. WOOLLINS, *Chem. Soc. Rev.* **21**, 245–52 (1992). T. M. KLAPÖTKE, in R. STEUDEL (ed.), *The Chemistry of Inorganic Ring Systems*, Elsevier, Amsterdam, 1992, pp. 409–27.
[128] H. FOLKERTS, B. NEUMÜLLER and K. DEHNICKE, *Z. anorg. allg. Chem.* **620**, 1011–15 (1994).

(1) $(Se_3N_2^{++})_2$

(2) $Se_3N_2^{2+}$

(3) $ClSe_3N_2^+$

(4) $[N(SeCl_2)_2]^+$

(5) $Se(NSO)_2$

(6) $ClSe_2N_2S^+$

(7) $Cl_2Se_2N_2S$

(8) $[S_3SeN_5]^+$

5-membered $\overline{Pt-SeNSeN}$ heterocycle at the planar Pt centre.[129] A similar reaction with [Pt(PPh₃)₃] in CH₂Cl₂ gives the analogous PPh₃ complex plus the related dark-green dimer, $[(Ph_3P)Pt(\mu,\eta^2-Se_2N_2)_2Pt(PPh_3)]$, in which the chelating ligand also bridges the two Pt atoms via the ipso-N atoms so as to form a central planar Pt_2N_2 core which is also coplanar with the two planar 5-membered heterocycles.[130] Innumerable other Se/N species have been synthesized and characterized by X-ray diffraction analysis, e.g. the 7π-electron radical cation $Se_3N_2^{\ddot{+}}$ (1),[131] the 6π-electron dication $Se_3N_2^{2+}$ (2),[131] $ClSe_3N_2$ (3),[132] $[N(SeCl_2)_2]^+$ (4),[133] $Se(NSO)_2$ (5),[134] $ClSe_3N_2S^+$ (6),[134] $Cl_2Se_2N_2S$ (7),[134] $[S_3SeN_5]^+$ (8),[134] etc. The original papers should be consulted for preparative procedures.

Metal complexes with Se/N ligands are also appearing in increasing numbers in the literature. Thus, $cyclo\text{-}Se_4N_2$ forms the red-brown donor–acceptor complexes $[SnCl_4(\eta^1\text{-}N_2Se_4)_2]$ (9) and $[TiCl_4(\eta^2\text{-}N_2Se_4)]$,[135] whereas reaction of $[Se_2SN_2]_2Cl_2$ with $cis\text{-}[PtCl_2(PMe_2Ph)_2]$ in liquid ammonia gives $[Pt(\eta^2\text{-}SeSN_2)(PMe_2Ph)_2]$ which in turn can be protonated with HBF₄ to give $[Pt(\eta^2\text{-}SeSN_2H)(PMe_2Ph)_2]^+$ (10).[136] The di-Se analogues with $\eta^2\text{-}Se_2N_2^{2-}$ and $\eta^2\text{-}Se_2N_2H^-$ have also been characterized.[137]

Heterocycles involving P^V include [1,5-(Ph₂P)₂N₄(SeMe)₂] (11), which has an 8-membered chair configuration with the two Se atoms displaced on either side of the P_2N_4 plane, and the related [1,5-(Ph₂P)₂N₄Se₂] (12).[138] The reaction of (12) with [PtCl₂(PEt₃)₂] gives the η^1-complexes (13), (14) which, in turn, can be oxidatively added to $[Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2]$ to give the $\eta^2\text{-}Se,Se'$ complexes (15) and (16),[139]

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

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

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

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

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

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

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

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

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

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

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

(9) $[SnCl_4(N_2Se_4)_2]$

(10) $[Pt(SeSN_2H)(PMe_2Ph)_2]^+$

(11) $[(Ph_2P)_2N_4(SeMe)_2]$

(12) $[(Ph_2P)_2N_4Se_2]$

(13)

(14)

(15)

(16)

(17) $P_2Se_8{}^{2-}$

(18) $[Fe_2(CO)_4(PSe_5)_2]$

Reaction of P_4Se_4 with soluble polyselenides afforded the first isolated P/Se anion, the yellow $P_2Se_8{}^{2-}$ (17) which further reacts with $Fe(CO)_5$ to generate the novel brown cluster anion $[Fe_2(CO)_4(PSe_5)_2]$ (18).[140] Numerous other examples are known; indeed, the whole field is still rapidly developing and many new types of compound are being synthesized and characterized each year.

Tellurium-chalcogen-nitrogen chemistry is also burgeoning. Typical examples include the red crystalline $Te(NSO)_2$,[141] isomorphous with $Se(NSO)_2$ (5), and the cationic heterocycle $[F\overline{TeNSNSeNSN}]^+[TeF_5]^-$, which is formed, together with $[\{\overline{SeNSNSe^•}\}_2]^{2+}[TeF_5]^-{}_2$, when $Se(NSO)_2$ reacts with TeF_4 in CH_2Cl_2.[142] The first stable tellurophosphorane complexes $[M(CO)_5(Te{=}PBu^t_3)]$ ($M = Cr$, Mo, W) were prepared as dark-red crystals by photolysis of the hexacarbonyls in the presence of $Bu^t_3P{=}Te$, and the expected bent coordination at Te was confirmed by X-ray analysis (angle W–Te–P 120.1°.[143] By Contrast, reaction of $Et_3P{=}Te$ with $[Mn(CH_2Ph)(CO)_5]$ in refluxing toluene results in the insertion of Te into

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

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

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

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

Reaction scheme for the formation of organo-selenium compounds (X = halogen).

the $Mn-CH_2$ bond and the displacement of two CO ligands to yield the red crystalline solid $[Mn(CO)_3(PEt_3)_2(TeCH_2Ph)]$, in which the three carbonyls are *mer* and the two tertiary phospine ligands are *trans* to each other.[144]

The increasing basicity of the heavier members of Group 16 is reflected in the increasing incidence of oxoacid salts. Thus polonium forms $Po(NO_3)_4.xN_2O_4$, $Po(SO_4)_2.xH_2O$, and a basic sulfate and selenate $2PoO_2.SO_3$ and $2PoO_2.SeO_3$ all of which are white, and a hydrated yellow chromate $Po(CrO_4)_2.xH_2O$. There is also fragmentary information on the precipitation of an insoluble polonium(IV) carbonate, iodate, phosphate and vanadate.[4] Tellurium(IV) forms a white basic nitrate $2TeO_2.HNO_3$ and a basic sulfate and selenate $2TeO_2.XO_3$, and there are indications of a white, hygroscopic basic sulfate of selenium(IV), $SeO_2.SO_3$ or $SeOSO_4$. Most of these compounds have been prepared by evaporation of aqueous solutions of the oxide or hydrated oxide in the appropriate acid. There is no doubt that more imaginative nonaqueous synthetic routes could be devised, but the likely products seem rather uninteresting and the field has attracted little recent attention.

16.2.8 Organo-compounds [145-149]

Organoselenium and organotellurium chemistry is a large and expanding field which parallels but is distinct from organosulfur chemistry. The biochemistry of organoselenium compounds has also been much studied (p. 759). Organopolonium chemistry is almost entirely restricted to trace-level experiments because of the charring and decomposition of the compounds by the intense α activity of polonium (pp. 749ff.).

The principal classes of organoselenium compound are summarized in the scheme above which indicates the central synthetic role of

144 K. McGregor, G. B. Deacon, R. S. Dickson, G. D. Fallon, R. S. Rowe and B. O. West, *J. Chem. Soc., Chem. Commun.*, 1293–4 (1990).

145 K. J. Irgolic and M. V. Kudchadker, The organic chemistry of selenium, Chap. 8 in ref. 2, pp. 408–545. H. E. Ganther, Biochemistry of selenium, Chap. 9 in ref. 2, pp. 546–614. W. C. Cooper and J. R. Glover, The toxicology of selenium and its compounds, Chap. 11 in ref. 2, pp. 654–74.

146 R. A. Zingaro and K. Irgolic, Organic compounds of tellurium, Chap 5 in ref. 3, pp. 184–280. W. C. Cooper. Toxicology of tellurium and its compounds, Chap. 7 in ref. 3, pp. 313–72.

147 P. D. Magnus, Organic selenium and tellurium compounds, in D. Barton and W. D. Ollis (eds.), *Comprehensive Organic Chemistry*, Vol. 3, Chap. 12, pp. 491–538, Pergamon Press, Oxford, 1979.

148 Specialist Periodical Reports of the Chemical Society (London), *Organic Compounds of Sulfur, Selenium and Tellurium*, Vols. 1–5 (1970–79).

149 S. Patai and Z. Rappaport (eds.) *The Chemistry of Organic Selenium and Tellurium Compounds*, John Wiley (Interscience), Chichester, Vol. 1, 1986, 939 pp. Vol. 2 (S. Patai, ed.), 1987, 864 pp.

(a) Me_3SeI

(b) $[TeMe_3]^+$

(c) $[Ph_3TeCl]_2$

(d) Structural units in $[TeMe_3]^+[TeMeI_4]^-$

(e) $Me_2TeI_2.I_2$

($\angle I(1)TeI(2)$ 175°)

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

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

Tellurocarbonyl derivatives $R^1C(=Te)OR^2$ and telluroamides, e.g. $PhC(=Te)NMe_2$ (mp 73°) have been prepared[150] and shown to be similar to, though more reactive than, the corresponding seleno derivatives.

Reaction of $[Se_4]^{2+}[AsF_6]_2^-$ with Ph_2Se_2 in liquid SO_2 gives the bright orange compound $[Se_6Ph_2]^{2+}[AsF_6]_2^-.SO_2$ in which the Se_6 ring adopts the boat conformation with pendent Ph groups in the 1- and 4-positions.[151] By contrast the reaction of K_2CO_3 with red-Se in acetone in

the presence of $[(Ph_3P)_2N]Cl$ yields red crystals of $[(Ph_3P)_2N]^+[Se_5C(Se)C(O)Me]^-$; the anion, which adopts the chair conformation, is the first example of an Se_5C ring, and the C atom has exocyclic $=Se$ and $-C(O)Me$ groups attached.[152]

Stoichiometry is frequently an inadequate guide to structure in organo-derivatives of Se and Te particularly when other elements (such as halogens) are also present. This arises from the incipient tendency of many of the compounds to undergo ionic dissociation or, conversely, to increase the coordination number of the central atom by dimerization or other oligomeric interactions. Thus Me_3SeI features pyramidal ions $[SeMe_3]^+$ but these are each associated rather closely with 1 iodide which is colinear with 1 Me–Se bond to give a distorted pseudotrigonal bipyramidal configuration (Fig. 16.18a).[125] A regular pyramidal cation can, however, be obtained by use of a large non-coordinating counteranion, as in

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

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

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

$[TeMe_3]^+[BPh_4]^-$ (Fig. 16.18b).[153] By contrast, Ph_3TeCl is a chloride-bridged dimer with 5-coordinate square-pyramidal Te (Fig. 16.13c).[154] The possibility of isomerism also exists: e.g. 4-coordinate, monomeric molecular Me_2TeI_2 and its ionic counterpart $[TeMe_3]^+[TeMeI_4]^-$ in which interionic interactions make both the cation and the anion pseudo-6-coordinate (Fig. 16.18d).[125] Further complications obtrude when the halogen itself is capable of forming polyhalide units in the crystal. Thus reaction of molecular Me_2TeI_2 with iodine readily affords Me_2TeI_4 but the chemical behaviour and spectra of the product give no evidence for oxidation to Te(VI), and X-ray analysis indicates the formation of an adduct $Me_2TeI_2.I_2$ in which the axially disposed iodine atoms of the pseudo-trigonal-bipyramidal Me_2TeI_2 are weakly bonded to molecules of iodine to form a network as shown in Fig. 16.18e[155] (cf. TlI_3, p. 239).

Among the range of homoleptic organotellurium compounds that have recently been synthesized are the perfluoroalkyl derivatives $Te(C_nF_{2n+1})_4$, $(n = 1-4)$.[156] Of these, the yellow oily liquid $Te(CF_3)_4$ is the least stable, being both light- and temperature-sensitive. It reacts with fluorides to give the complex anion $[Te(CF_3)_4F]^-$ and with fluoride-ion acceptors to form the cation $[Te(CF_3)_3]^+$. $Te(CF_3)_4$ is made by reacting $Te(CF_3)_2Cl_2$ with $Cd(CF_3)_2$ in MeCN. The higher members can be made directly form $TeCl_4$ and $Cd(CF_3)_2$ are also viscous yellow liquids. The related $TeMe_4$ was first made in 1989 as a yellow pyrophoric liquid by treating $TeCl_4$ with LiMe in ether at $-78°$;[157] it can be oxidized by XeF_2 to the volatile white solid Me_4TeF_2 which, when treated with $ZnMe_2$, gave $TeMe_6$ as a white

solid.[158] $TeMe_6$, the first peralkylated derivative of a hexavalent main-group element, can be heated for several hours at $140°$ without decomposition, and is thus much more stable than $TeMe_4$.

(19) $F_2C(\mu\text{-}Te)_2CF_2$

Organopolytellurides (and polyselenides) are also known, e.g. ArTeTeAr (Ar $= 2, 4, 6$-$Ph_3C_6H_2$-)[159] and RTeTeTeR (R $= (Me_3Si)_3$-C);[160] the stabilizing rôle of the bulky end groups is evident. [The related "isoelectronic" cation $Bu^t_3PTeTeTePBu^t_3{}^{2+}$ can also be noted;[161] it is prepared by oxidizing the tellurophosphorane $Bu^t_3P=Te$ (see p. 785) using ferricenium salts.] Related compounds are R_2Se_x $(x = 2-7)$ and $(RSe)_2S_y$ $(y = 1-15)$.[162] Other compounds of note are the first "telluroketone", $Te=CF_2$,[163] a thermally unstable violet compound which readily dimerizes even below room temperature to the dark-red crystalline 1,3-ditelluretane (19). Cocondensation with its analogue, $Se=CF_2$ yields the corresponding volatile orange solid, 1-selena-3-telluretane, $F_2\overline{CTeCF_2S}e$.

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

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

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

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

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

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

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

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

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

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

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