

Molten Pb reacts with the chalcogens to give PbS, PbSe and PbTe.

The steady trend towards increasing stability of M^{II} rather than M^{IV} compounds in the sequence Ge, Sn, Pb is an example of the so-called "inert-pair effect" which is well established for the heavier post-transition metals. The discussion on p. 226 is relevant here. A notable exception is the organometallic chemistry of Sn and Pb which is almost entirely confined to the M^{IV} state (pp. 399–405).

Catenation is also an important feature of the chemistry of Ge, Sn and Pb though less so than for C and Si. The discussion on p. 341 can be extended by reference to the bond energies in Table 10.3 from which it can be seen that there is a steady decrease in the M–M bond strength. In general, with the exception of M–H bonds, the strength of other M–X bonds diminishes less noticeably, though the absence of Ge analogues of silicone polymers speaks for the lower stability of the Ge–O–Ge linkage.

The structural chemistry of the Group 14 elements affords abundant illustrations of the trends to be expected from increasing atomic size, increasing electropositivity and increasing tendency to form M^{II} compounds, and these will become clear during the more detailed treatment of the chemistry in the succeeding sections. The often complicated stereochemistry of M^{II} compounds (which arises from the presence of a nonbonding electron-pair on the metal) is

particularly revealing as also is the propensity of Sn^{IV} to become 5- and 6-coordinate.⁽¹⁴⁾ The ability of both Sn and Pb to form polyatomic cluster anions of very low formal oxidation state, (e.g. M_5^{2-} , M_9^{4-} , etc.) reflects the now well-established tendency of the heavier post-transition elements to form chain, ring or cluster homopolyatomic ions:⁽¹⁸⁾ this was first established for the polyhalide anions and for Hg_2^{2+} but is also prevalent in Groups 14, 15 and 16, e.g. Pb_9^{4-} is isoelectronic with Bi_9^{5+} (see Section 10.3.6, p. 391).

10.3 Compounds

10.3.1 Hydrides and hydrohalides

Germanes of general formula Ge_nH_{2n+2} are known as colourless gases or volatile liquids for $n = 1-5$ and their preparation, physical properties, and chemical reactions are very similar to those of silanes (p. 337). Thus GeH_4 was formerly made by the inefficient hydrolysis of Mg/Ge alloys with aqueous acids but is now generally made by the reaction of $GeCl_4$ with $LiAlH_4$ in ether or even more conveniently by the reaction of GeO_2 with aqueous solutions of $NaBH_4$. The higher germanes are prepared by the action of a silent electric discharge on GeH_4 ; mixed hydrides such as SiH_3GeH_3 can be prepared similarly by circulating a mixture of SiH_4 and GeH_4 but no cyclic or unsaturated hydrides have yet been prepared. The germanes are all less volatile than the corresponding silanes (see Table) and, perhaps surprisingly,

Table 10.3 Approximate average bond energies/ $\text{kJ mol}^{-1(a)}$

M–	–M	–C	–H	–F	–Cl	–Br	–I
C	356	356	416	490	325	279	216
Si	226	360	323	596	400	325	248
Ge	188	255	289	471	339	281	216
Sn	151	226	253	—	315	261	187
Pb	98	130	205	411	308	—	—

^(a)These values often vary widely (by as much as $50-100 \text{ kJ mol}^{-1}$) depending on the particular compound considered and the method of computation used. Individual values are thus less significant than general trends. The data represent a collation of values for typical compounds gleaned from refs 15–17.

¹⁴ J. A. ZUBIETA and J. J. ZUCKERMAN, Structural tin chemistry, *Prog. Inorg. Chem.* **24**, 251–475 (1978). An excellent comprehensive review with full structural diagrams and data, and more than 750 references.

¹⁵ J. A. KERR, Bond strengths in polyatomic molecules, *CRC Handbook of Chemistry and Physics*, 73rd edn., 1992–3, pp. 9.138–9.145.

¹⁶ W. E. DASENT, *Inorganic Energetics*, 2nd edn., Cambridge Univ. Press, 1982, 185 pp.

¹⁷ C. F. SHAW and A. L. ALLRED, *Organometallic Chem. Rev.* **5A**, 95–142 (1970).

¹⁸ J. D. CORBETT, *Prog. Inorg. Chem.* **21**, 129–55 (1976).

Property	GeH ₄	Ge ₂ H ₆
MP/°C	-164.8	-109
BP/°C	-88.1	29
Density (T°C)/g cm ⁻³	1.52 (-142°)	1.98 (-109°)

Property	Ge ₃ H ₈	Ge ₄ H ₁₀	Ge ₅ H ₁₂
MP/°C	-105.6	-	-
BP/°C	110.5	176.9	234
Density (T°C)/g cm ⁻³	2.20 (-105°)	-	-

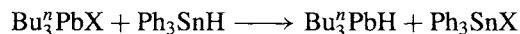
noticeably less reactive. Thus, in contrast to SiH₄ and SnH₄, GeH₄ does not ignite in contact with air and is unaffected by aqueous acid or 30% aqueous NaOH. It acts as an acid in liquid NH₃ forming NH₄⁺ and GeH₃⁻ ions and reacts with alkali metals in this solvent (or in MeOC₂H₄-OMe) to give MGeH₃. Like the corresponding MSiH₃, these are white, crystalline compounds of considerable synthetic utility. X-ray diffraction analysis shows that KGeH₃ and RbGeH₃ have the NaCl-type structure, implying free rotation of GeH₃⁻, and CsGeH₃ has the rare TII structure (p. 242). The derived "ionic radius" of 229 pm emphasizes the similarity to SiH₃⁻ (226 pm) and this is reinforced by the bond angles deduced from broad-line nmr experiments: SiH₃⁻ 94 ± 4° (cf. isoelectronic PH₃, 93.5°); GeH₃⁻ 92.5 ± 4° (cf. isoelectronic AsH₃, 91.8°).⁽¹⁹⁾

The germanium hydrohalides GeH_xX_{4-x} (X = Cl, Br, I; x = 1, 2, 3) are colourless, volatile, reactive liquids. Preparative routes include reaction of Ge, GeX₂ or GeH₄ with HX. The compounds are valuable synthetic intermediates (cf. SiH₃I). For example, hydrolysis of GeH₃Cl yields O(GeH₃)₂, and various metatheses can be effected by use of the appropriate Ag salts or, more effectively, Pb^{II} salts, e.g. GeH₃Br with PbO, Pb(OAc)₂, and Pb(NCS)₂ affords O(GeH₃)₂, GeH₃(OAc), and GeH₃(SCN). Treatment of this latter compound with MeSH or [Mn(CO)₅H] yields GeH₃SMe

and [Mn(CO)₅(GeH₃)] respectively. An extensive phosphinogermane chemistry is also known, e.g. R_nGe(PH₂)_{4-n}, R = alkyl or H. The novel germimine CF₃N=GeH₂ has been obtained as a colourless gas by reacting a 1:1 mixture of GeH₄ and CF₃NO in a sealed tube at 120° (the other product being H₂O). Addition of HI to the Ge=N double bond gave CF₃NHGeH₂I.⁽²⁰⁾

Binary Sn hydrides are much less stable. Reduction of SnCl₄ with ethereal LiAlH₄ gives SnH₄ in 80–90% yield; SnCl₂ reacts similarly with aqueous NaBH₄. SnH₄ (mp -146°, bp -52.5°) decomposes slowly to Sn and H₂ at room temperature; it is unattacked by dilute aqueous acids or alkalis but is decomposed by more concentrated solutions. It is a potent reducing agent. Sn₂H₆ is even less stable, and higher homologues have not been obtained. By contrast, organotin hydrides are more stable, and catenation up to H(SnPh₂)₆H has been achieved by thermolysis of Ph₂SnH₂. Preparation of R_nSnH_{4-n} is usually by LiAlH₄ reduction of the corresponding organotin chloride.

PbH₄ is the least well-characterized Group 14 hydride and it is unlikely that it has ever been prepared except perhaps in trace amounts at high dilution; methods which successfully yield MH₄ for the other Group 14 elements all fail even at low temperatures. The alkyl derivatives R₂PbH₂ and R₃PbH can be prepared from the corresponding halides and LiAlH₄ at -78° or by exchange reactions with Ph₃SnH, e.g.:



Me₃PbH (mp ~ -106°, decomp above -30°) and Et₃PbH (mp ~ -145°, decomp above -20°) readily add to alkenes and alkynes (hydroplumbation) to give stable tetraorganolead compounds.

10.3.2 Halides and related complexes

Germanium, Sn and Pb form two series of halides: MX₂ and MX₄. PbX₂ are more stable than PbX₄, whereas the reverse is

¹⁹ G. THIRASE, E. WEISS, H. J. HENNING and H. LECHERT, *Z. anorg. allg. Chem.* **417**, 221–8 (1975).

²⁰ H. G. ANG and F. KLEE, *J. Chem. Soc., Chem. Commun.*, 310–12 (1989).

true for Ge, consistent with the steady increase in stability of the dihalides in the sequence $CX_2 \ll SiX_2 < GeX_2 < SnX_2 < PbX_2$. Numerous complex halides are also known for both oxidation states.

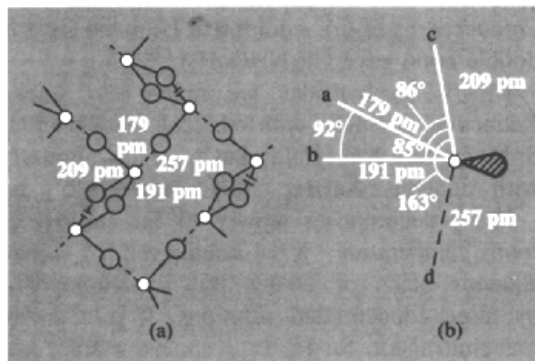
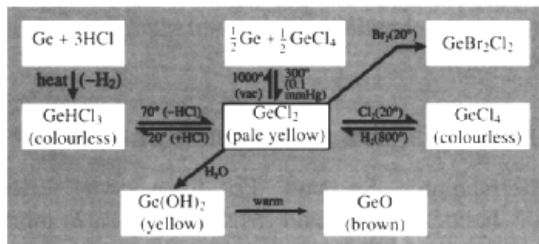


Figure 10.2 Crystal structure of GeF_2 : (a) projection along the chains, and (b) environment of Ge (pseudo trigonal bipyramidal). The bond to the unshared F is appreciably shorter (179 pm) than those in the chain and there is a weaker interaction (257 pm) linking the chains into a 3D structure.

Germanium halides

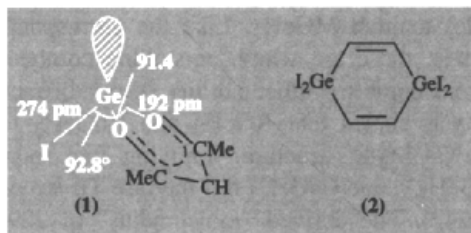
GeF_2 is formed as a volatile white solid (mp 110°) by the action of GeF_4 on powdered Ge at 150 – 300° ; it has a unique structure in which trigonal pyramidal $\{GeF_3\}$ units share 2 F atoms to form infinite spiral chains (Fig. 10.2). Pale-yellow $GeCl_2$ can be prepared similarly at 300° or by thermal decomposition of $GeHCl_3$ at 70° . Typical reactions are summarized in the scheme:



$GeBr_2$ is made by reduction of $GeBr_4$ or $GeHBr_3$ with Zn, or by the action of HBr on an excess of Ge at 400° ; it is a yellow solid, mp 122° ,

which disproportionates to Ge and $GeBr_4$ at 150° , adds HBr at 40° , and hydrolyses to the unstable yellow $Ge(OH)_2$. GeI_2 is best prepared by reduction of GeI_4 with aqueous H_3PO_2 in the presence of HI to prevent hydrolysis; it sublimes to give bright orange-yellow crystals, is stable in dry air and disproportionates only when heated above $\sim 550^\circ$. The structure of the lemon-yellow, monomeric, pyramidal 3-coordinate Ge^{II} complex $[Ge(acac)I]$ (1) has been determined.⁽²¹⁾ GeI_2 is oxidized to GeI_4 in aqueous KI/HCl; it forms numerous adducts with nitrogen ligands, and reacts with C_2H_2 at 140° to give a compound that was originally formulated as a

3-membered heterocycle $\begin{array}{c} CH \\ || \\ CH \end{array} \rangle GeI_2$ but which was subsequently shown by mass spectroscopy to have the unusual dimeric structure (2).



The ternary Ge^{II} halides, $MGeX_3$ ($M = Rb, Cs; X = Cl, Br, I$) are polymorphic with various distorted perovskite-like (p. 963) structures which reflect the influence of the “non-bonding” pair of electrons on the Ge^{II} centre.⁽²²⁾ Thus, at room temperature, rhombohedral $CsGeI_3$ has three Ge–I at 275 pm and three at 327 pm whereas in the high-temperature cubic form (above $277^\circ C$) there are six Ge–I distances at 320 pm as a result of position changes of the Ge atoms (reversible order–disorder transition). Again, $RbGeI_3$ has a lemon-yellow, orthorhombic form below -92° ; an intermediate, bordeaux-red orthorhombic perovskite form (-92° to -52°); a black rhombohedral form (-52° to -29°); and

²¹ S. R. STOBART, M. R. CHURCHILL, F. J. HOLLANDER and W. J. YOUNGS, *J. Chem. Soc., Chem. Commun.*, 911–12 (1979).

²² G. THIELE, H. W. ROTTER and K. D. SCHMIDT, *Z. anorg. allg. Chem.* **545**, 148–56 (1987); **571**, 60–8 (1989).

a black, cubic perovskite form between -29° and the decomposition temperature, $+61^\circ$. In the yellow form there is one Ge–I at 281 pm, four at 306 pm and one at 327 pm, whereas in the red form there are three Ge–I at 287 pm and three at 324 pm. All the compounds are readily made simply by heating $\text{Ge}(\text{OH})_2$ with MX in aqueous HX solutions.

Germanium tetrahalides are readily prepared by direct action of the elements or via the action of aqueous HX on GeO_2 . The lighter members are colourless, volatile liquids, but GeI_4 is an orange solid (cf. CX_4 , SiX_4). All hydrolyse readily and GeCl_4 in particular is an important intermediate in the preparation of organogermanium compounds via LiR or RMgX reagents. Many mixed halides and hydrohalides are also known, as are complexes of the type GeF_6^{2-} , GeCl_6^{2-} , *trans*- L_2GeCl_4 and L_4GeCl_4 (L = tertiary amine or pyridine). The curious mixed-valency complex Ge_3F_{12} , i.e. $[(\text{GeF}_2)_4\text{GeF}_4]$ has been shown to feature distorted square pyramids of $\{\text{:Ge}^{\text{II}}\text{F}_4\}$ with the “lone-pair” of electrons pointing away from the 4 basal F atoms which are at 181, 195, 220, and 245 pm from the apical Ge^{II} ; the Ge^{IV} atom is at the centre of a slightly distorted octahedron ($\text{Ge}^{\text{IV}}\text{–F}$ 171–180 pm, angle F–Ge–F $87.5\text{--}92.5^\circ$) and the whole structure is held together by F bridges.⁽²³⁾

Property	GeF_4	GeCl_4
MP/ $^\circ\text{C}$	-15 (4 atm)	-49.5
BP/ $^\circ\text{C}$	-36.5 (subl)	83.1
Density ($T^\circ\text{C}$)/ g cm^{-3}	2.126 (0°)	1.844 (30°)
Property	GeBr_4	GeI_4
MP/ $^\circ\text{C}$	26	146
BP/ $^\circ\text{C}$	186	~ 400
Density ($T^\circ\text{C}$)/ g cm^{-3}	2.100 (30°)	4.322 (26°)

Tin halides

The structural chemistry of Sn^{II} halides is particularly complex, partly because of the

stereochemical activity (or non-activity) of the nonbonding pair of electrons and partly because of the propensity of Sn^{II} to increase its CN by polymerization into larger structural units such as rings or chains. Thus, the first and second ionization energies of Sn (p. 372) are very similar to those of Mg (p. 111), but Sn^{II} rarely adopts structures typical of spherically symmetrical ions because the nonbonding pair of electrons, which is $5s^2$ in the free gaseous ion, readily distorts in the condensed phase; this can be described in terms of ligand-field distortions or the adoption of some “p character”. Again, the “nonbonding” pair can act as a donor to vacant orbitals, and the “vacant” third 5p orbital and 5d orbitals can act as acceptors in forming further covalent bonds. A good example of this occurs with the adducts $[\text{SnX}_2(\text{NMe}_3)]$ (X = Cl, Br, I): the Sn^{II} atom, which has accepted a pair of electrons from the ligand NMe_3 , can itself donate its own lone-pair to a strong Lewis acid to form a double adduct of the type $[\text{BF}_3\{\leftarrow\text{SnX}_2(\leftarrow\text{NMe}_3)\}]$ (X = Cl, Br, I).⁽²⁴⁾ Further examples, including more complicated interactions, are described later in this subsection.

SnF_2 (which is obtained as colourless monoclinic crystals by evaporation of a solution of SnO in 40% aqueous HF) is composed of Sn_4F_8 tetramers interlinked by weaker Sn–F interactions;⁽²⁵⁾ the tetramers are puckered 8-membered rings of alternating Sn and F as shown in Fig. 10.3 and each Sn is surrounded by a highly distorted octahedron of F (1 Sn– F_t at ~ 205 pm, 2 Sn– F_μ at ~ 218 pm, and 3 much longer Sn \cdots F in the range 240–329 pm, presumably due to the influence of the nonbonding pair of electrons. In aqueous solutions containing F^- the predominant species is the very stable pyramidal complex SnF_3^- but crystallization is attended by further condensation. For example, crystallization of SnF_2 from aqueous solutions containing NaF does not give NaSnF_3 as previously supposed but

²⁴ C. C. HSU and R. A. GEANANGEL, *Inorg. Chem.* **19**, 110–9 (1980).

²⁵ R. C. McDONALD, H. HO-KUEN HAU and K. ERIKS, *Inorg. Chem.* **15**, 762–5 (1976).

²³ J. C. TAYLOR and P. W. WILSON, *J. Am. Chem. Soc.* **95**, 1834–8 (1973).

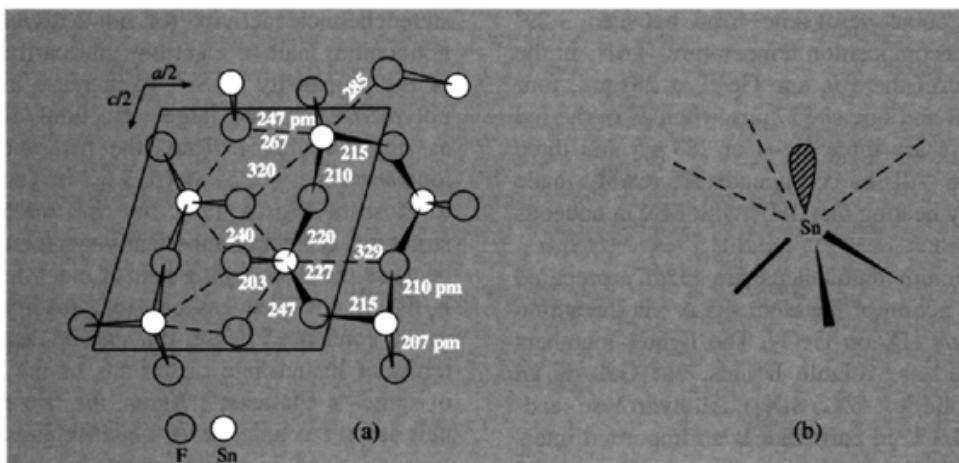


Figure 10.3 Structure of SnF_2 showing (a) interconnected rings of $\{\text{Sn}_4\text{F}_4(\text{F}_4)\}$, and (b) the unsymmetrical 3 + 3 coordination around Sn.

NaSn_2F_5 or $\text{Na}_4\text{Sn}_3\text{F}_{10}$ depending on conditions. The $\{\text{Sn}_2\text{F}_5\}$ unit in the first compound can be thought of as a discrete ion $[\text{Sn}_2\text{F}_5]^-$ or as an F^- ion coordinating to 2 SnF_2 molecules (Fig. 10.4a): each Sn is trigonal pyramidal with two close F_1 , one intermediate F_μ , and 3 more distant F at 253, 298, and

301 pm. By contrast the compound $\text{Na}_4\text{Sn}_3\text{F}_{10}$ features 3 corner-shared square-pyramidal $\{\text{SnF}_4\}$ units (Fig. 10.4b) though the wide range of Sn-F distances could be taken to indicate incipient formation of a central SnF_4^{2-} weakly bridged to two terminal SnF_3^- groups. In the corresponding system with KF the compound

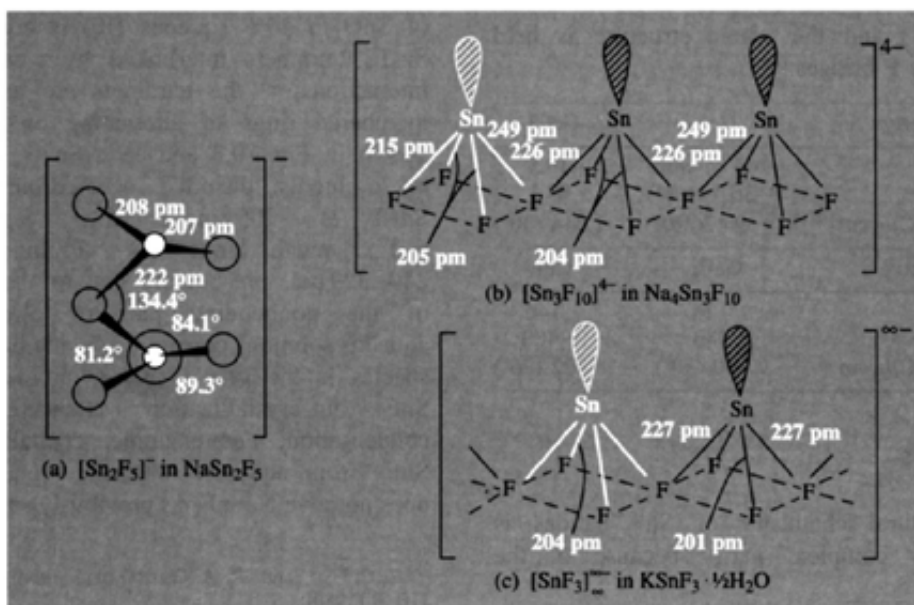


Figure 10.4 Structure of some fluoro-complexes of Sn^{II} .

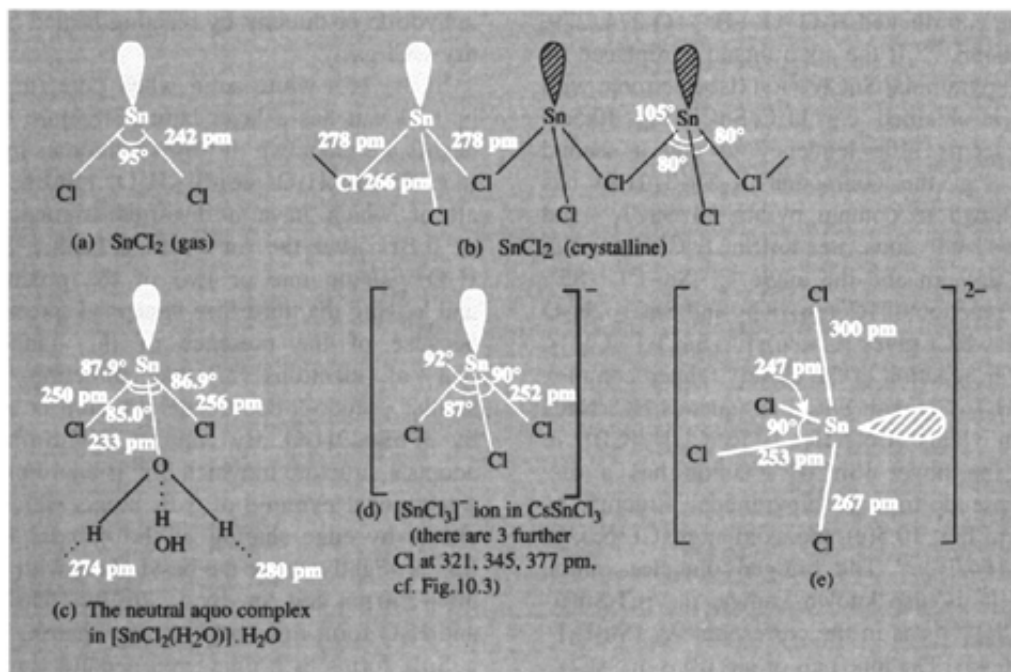


Figure 10.5 Structure of SnCl_2 and some chloro complexes of Sn^{II} .

that crystallizes is $\text{KSnF}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ in which the bridging of square pyramids is extended to give infinite chain polymers (Fig. 10.4c). (The main commercial application of SnF_2 is in toothpaste and dental preparations where it is used to prevent demineralization of teeth and to lessen the development of dental caries.)

SnF_4 is described on p. 381. There are also some intriguing mixed valence compounds such as Sn_3F_8 (i.e. $\text{Sn}_2^{\text{II}}\text{Sn}^{\text{IV}}\text{F}_8$) which is formed when solutions of SnF_2 in anhydrous HF are oxidized at room temperature with F_2 , O_2 or even SO_2 ; the structure features nearly regular $\{\text{Sn}^{\text{IV}}\text{F}_6\}$ octahedra *trans*-bridged to $\{\text{Sn}^{\text{II}}\text{F}_3\}$ pyramids which themselves form polymeric $\text{Sn}^{\text{II}}\text{F}$ chains: $\text{Sn}^{\text{IV}}\text{-F}$ 196 pm and $\text{Sn}^{\text{II}}\text{-F}$ 210, 217, 225 pm with weaker $\text{Sn}^{\text{II}}\cdots\text{F}$ interactions in the range 255–265 pm.⁽²⁶⁾ Another example is $\alpha\text{-Sn}_2\text{F}_6$ (i.e. $\text{Sn}^{\text{II}}\text{Sn}^{\text{IV}}\text{F}_6$) which transforms to $\beta\text{-Sn}_2\text{F}_6$ at 112° and to $\gamma\text{-Sn}_2\text{F}_6$ at 197° .

High-temperature neutron diffraction studies⁽²⁷⁾ have shown that this latter phase has the cubic ordered ReO_3 -type structure (p. 1047) with octahedral coordination of both types of Sn atoms by F ($\text{Sn}^{\text{II}}\text{-F}$ 229 pm, $\text{Sn}^{\text{IV}}\text{-F}$ 186 pm). The β -phase also features octahedral coordination in a structure closely related to that of rhombohedral LiSbF_6 .

Tin(II) chlorides are similarly complex (Fig. 10.5). In the gas phase, SnCl_2 forms bent molecules, but the crystalline material (mp 246° , bp 623°) has a layer structure with chains of corner-shared trigonal pyramidal $\{\text{SnCl}_3\}$ groups. The dihydrate also has a 3-coordinated structure with only 1 of the H_2O molecules directly bonded to the Sn^{II} (Fig. 10.5c); the neutral aquo complexes are arranged in double layers with the second H_2O molecules interleaved between them to form a two-dimensional H-bonded network

²⁶ M. F. A. DOVE, R. KING and T. J. KING, *J. Chem. Soc., Chem. Commun.*, 944–5 (1973).

²⁷ M. RUCHAUD, C. MIRAMBET, L. FOURNES, J. GRANNEC and J. L. SOUBEYROUX, *Z. anorg. allg. Chem.* **590**, 173–80 (1990).

with the coordinated H_2O ($\text{O}-\text{H}\cdots\text{O}$ 274, 279, and 280 pm.⁽²⁸⁾ If the aquo ligand is replaced by Cl^- the pyramidal SnCl_3^- ion (isoelectronic with SbCl_3) is obtained, e.g. in CsSnCl_3 Fig. 10.5d). There seems little tendency to add a second ligand: e.g. the compound $\text{K}_2\text{SnCl}_4\cdot\text{H}_2\text{O}$ has been shown to contain pyramidal SnCl_3^- and "isolated" Cl^- ions, i.e. $\text{K}_2[\text{SnCl}_3]\text{Cl}\cdot\text{H}_2\text{O}$ with $\text{Sn}-\text{Cl}$ 259 pm and the angle $\text{Cl}-\text{Sn}-\text{Cl} \sim 85^\circ$. Again, reaction of $[\text{Co}(\text{en})_3]\text{Cl}_3$ and $\text{SnCl}_2\cdot 2\text{H}_2\text{O}$ in excess HCl gives $[\text{Co}(\text{en})_3]^{3+}[\text{SnCl}_3]^- (\text{Cl}^-)_2$. However, reaction of the closely related complex $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ with SnCl_2 in aqueous HCl/NaCl solution yields $[\text{Co}(\text{NH}_3)_6]^{3+}[\text{SnCl}_4]^{2-} (\text{Cl}^-)$ in which the novel $[\text{SnCl}_4]^{2-}$ anion has a distorted pseudo-trigonal bipyramidal structure as shown in Fig. 10.5(e), the axial angle $\text{Cl}-\text{Sn}-\text{Cl}$ being 164.7° .⁽²⁹⁾ The bridged dinuclear anion $[\text{Sn}_2\text{Cl}_5]^-$ is also known, i.e. $[\text{Cl}_2\text{Sn}(\mu\text{-Cl})\text{SnCl}_2]^-$ ⁽³⁰⁾ as in the corresponding $[\text{Sn}_2\text{F}_5]^-$ (Fig. 10.4a). The lone pair of electrons in SnCl_3^- can itself act as a ligating bond: for example, SnCl_3^- can replace PPh_3 from the central Au atom in the cluster cation $[\text{Au}_8(\text{PPh}_3)_8]^{2+}$ to give $[\text{Au}_8(\text{PPh}_3)_7(\text{SnCl}_3)]^+$.⁽³¹⁾ Another interesting system involves crown complexes (p. 96) such as $[\text{Sn}(18\text{-crown-6})\text{Cl}]^+[\text{SnCl}_3]^-$ in which the cation features 7-coordinate hexagonal-pyramidal Sn^{II} .⁽³²⁾

Apart from its structural interest, SnCl_2 is important as a widely used mild reducing agent in acid solution. The dihydrate is commercially available for use in electrolytic tin-plating baths, as a sensitizer in silvering mirrors and in the plating of plastics, and as a perfume stabilizer in toilet soaps. The anhydrous material can be obtained either by dehydration using acetic

anhydride or directly by reacting heated Sn with dry HCl gas.

SnBr_2 is a white solid when pure (mp 216° , bp 620°); it has a layer-lattice structure but the details are unknown. It forms numerous hydrates (e.g. $3\text{SnBr}_2\cdot\text{H}_2\text{O}$, $2\text{SnBr}_2\cdot\text{H}_2\text{O}$, $6\text{SnBr}_2\cdot 5\text{H}_2\text{O}$) all of which have a distorted trigonal prism of 6 Br about the Sn^{II} with a further Br and H_2O capping one or two of the prism faces and leaving the third face uncapped (presumably because of the presence of the nonbonding pair of electrons in that direction).⁽³³⁾ A similar pseudo-9-coordinate structure is adopted by $3\text{PbBr}_2\cdot 2\text{H}_2\text{O}$. By contrast, $\text{NH}_4\text{SnBr}_3\cdot\text{H}_2\text{O}$ adopts a structure in which Sn^{II} is coordinated by a tetragonal pyramid of 5 Br atoms which form chains by edge sharing of the 4 basal Br; the Sn^{II} is slightly above the basal plane with $\text{Sn}-\text{Br}$ 304–350 pm and $\text{Sn}-\text{Br}_{\text{apex}}$ 269 pm. The NH_4^+ and H_2O form rows between the chains.

SnI_2 forms as brilliant red needles (mp 316° , bp 720°) when Sn is heated with I_2 in 2 M hydrochloric acid. It has a unique structure in which one-third of the Sn atoms are in almost perfect octahedral coordination in rutile-like chains (2 Sn–I 314.7 pm, 4 Sn–I 317.4 pm, and no significant distortions of angles from 90°); these chains are in turn cross-linked by double chains containing the remaining Sn atoms which are themselves 7-coordinate (5 Sn–I all on one side at 300.4–325.1 and 2 more-distant I at 371.8 pm).⁽³⁴⁾ There is an indication here of reduced distortion in the octahedral site and this has been observed more generally for compounds with the heavier halides and chalcogenides in which the nonbonding electron pair on Sn^{II} can delocalize into a low-lying band of the crystal. Accordingly, SnTe is a metalloid with cubic NaCl structure. Likewise, $\text{CsSn}^{\text{II}}\text{Br}_3$ has the ideal cubic perovskite structure (p. 963);⁽³⁵⁾ the compound forms black lustrous crystals with a semi-metallic

²⁸ H. KIRIYAMA, K. KITAHAMA, O. NAKAMURA and R. KIRIYAMA, *Bull. Chem. Soc. Japan* **46**, 1389–95 (1973).

²⁹ H. J. HAUPT, F. HUBER and H. PREUT, *Z. anorg. allg. Chem.* **422**, 97–103 (1976).

³⁰ M. VEITH, B. GÜDICKE and V. HUCH, *Z. anorg. allg. Chem.* **579**, 99–110 (1989).

³¹ Z. DEMIDOWICZ, R. L. JOHNSTON, J. C. MACHELL, D. M. P. MINGOS and I. D. WILLIAMS, *J. Chem. Soc., Dalton Trans.*, 1751–6 (1988).

³² M. G. B. DREW and D. G. NICHOLSON, *J. Chem. Soc., Dalton Trans.*, 1543–9 (1986).

³³ J. ANDERSON, *Acta Chem. Scand.* **26**, 1730, 2543, 3813 (1973).

³⁴ R. A. HOWIE, W. MOSER and I. C. TREVENA, *Acta Cryst.* **B28**, 2965–71 (1972).

³⁵ J. D. DONALDSON, J. SILVER, S. HADJIMINOLIS and S. D. ROSS, *J. Chem. Soc., Dalton Trans.*, 1500–6 (1975) and

conductivity of $\sim 10^3 \text{ ohm}^{-1} \text{ cm}^{-1}$ at room temperature due, it is thought, to the population of a low-lying conduction band formed by the overlap of "empty" t_2 5d orbitals on Br. In this connection it is noteworthy that $\text{Cs}_2\text{Sn}^{\text{IV}}\text{Br}_6$ has a very similar structure to $\text{CsSn}^{\text{II}}\text{Br}_3$ (i.e. $\text{Cs}_2\text{Sn}_2^{\text{II}}\text{Br}_6$) but with only half the Sn sites occupied — it is white and non-conducting since there are no high-energy nonbonding electrons to populate the conduction band which must be present. Similarly, yellow $\text{CsSn}^{\text{II}}\text{I}_3$, $\text{CsSn}_2^{\text{II}}\text{Br}_5$, $\text{Cs}_4\text{Sn}^{\text{II}}\text{Br}_6$ and compositions in the system $\text{CsSn}_2^{\text{II}}\text{X}_5$ ($\text{X} = \text{Cl}, \text{Br}$) all transform to black metalloids on being warmed, and even yellow monoclinic CsSnCl_3 (Fig. 10.5d) transforms at 90° to a dark-coloured cubic perovskite structure. In solutions of SnX_2 in aqueous HX , however, the pyramidal SnX_3^- ions are formed and, by suitable mixtures of halides followed by extraction into Et_2O , all ten trihalogenostannate(II) anions $[\text{SnCl}_x\text{Br}_y\text{I}_z]^-$ ($x + y + z = 3$) have been observed and characterized by ^{119}Sn nmr spectroscopy.⁽³⁶⁾

Tin(IV) halides are more straightforward. SnF_4 (prepared by the action of anhydrous HF on SnCl_4) is an extremely hygroscopic, white crystalline compound which sublimes above 700° . The structure (unlike that of CF_4 , SiF_4 and GeF_4) is polymeric with octahedral coordination

Property	SnF_4	SnCl_4
Colour	White	Colourless
MP/ $^\circ\text{C}$	—	-33.3
BP/ $^\circ\text{C}$	~ 705 (subl)	114
Density ($T^\circ\text{C}$)/ g cm^{-3}	4.78 (20°)	2.234(20°)
Sn-X/pm	188, 202	231
Property	SnBr_4	SnI_4
Colour	Colourless	Brown
MP/ $^\circ\text{C}$	31	144
BP/ $^\circ\text{C}$	205	348
Density ($T^\circ\text{C}$)/ g cm^{-3}	3.340(35°)	4.56(20°)
Sn-X/pm	244	264

about Sn: the $\{\text{SnF}_6\}$ units are joined into planar layers by edge-sharing of 4 equatorial F atoms ($\text{Sn}-\text{F}_\mu$ 202 pm) leaving 2 further (terminal) F in *trans* positions above and below each Sn ($\text{Sn}-\text{F}_t$ 188 pm). The other SnX_4 can be made by direct action of the elements and are unremarkable volatile liquids or solids comprising tetrahedral molecules. Similarities with the tetrahalides of Si and Ge are obvious. The compounds hydrolyse readily but definite hydrates can also be isolated from acid solution, e.g. $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, $\text{SnBr}_4 \cdot 4\text{H}_2\text{O}$. Complexes with a wide range of organic and inorganic ligands are known, particularly the 6-coordinate *cis*- and *trans*- L_2SnX_4 and occasionally the 1:1 complexes LSnX_4 . Stereochemistry has been deduced by infrared and Mössbauer spectroscopy and, when possible, by X-ray crystallography. The octahedral complexes SnX_6^{2-} ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) are also well characterized for numerous cations. Five-coordinate trigonal bipyramidal complexes are less common but have been established for SnCl_5^- and $\text{Me}_2\text{SnCl}_3^-$. A novel rectangular pyramidal geometry for Sn^{IV} has been revealed by X-ray analysis of the spirocyclic dithiolato complex anion $[(\text{MeC}_6\text{H}_3\text{S}_2)_2\text{SnCl}]^-$: the Cl atom occupies the apical position and the Sn atom is slightly above the plane of the 4 S atoms (mean angle $\text{Cl}-\text{Sn}-\text{Cl}$ 103°).⁽³⁷⁾ A similar stereochemistry has also been established for Si^{IV} (p. 335) and for Ge^{IV} in $[(\text{C}_6\text{H}_4\text{O}_2)_2\text{GeCl}]^-$.

Lead halides

Lead continues the trends outlined in preceding sections, PbX_2 being much more stable thermally and chemically than PbX_4 . Indeed, the only stable tetrahalide is the yellow PbF_4 (mp 600°); PbCl_4 is a yellow oil (mp -15°) stable below 0° but decomposing to PbCl_2 and Cl_2 above 50° ; PbBr_4 is even less stable and PbI_4 is of doubtful existence (cf. discussion on TlI_3 , p. 239). Stability can be markedly increased by coordination: e.g.

1980-3 (1975); see also J. D. DONALDSON and J. SILVER, *J. Chem. Soc., Dalton Trans.*, 666-9 (1973).

³⁶ J. M. CODDINGTON and M. J. TAYLOR, *J. Chem. Soc., Dalton Trans.*, 2223-7 (1989).

³⁷ A. C. SAU, R. O. DAY and R. R. HOLMES, *Inorg. Chem.* **20**, 3076-81 (1981); *J. Am. Chem. Soc.* **102**, 7972-3 (1980).

direct chlorination of PbCl_2 in aqueous HCl followed by addition of an alkali metal chloride gives stable yellow salts M_2PbCl_6 ($\text{M} = \text{Na}, \text{K}, \text{Rb}, \text{Cs}, \text{NH}_4$) which can serve as a useful source of Pb^{IV} . By contrast, PbX_2 are stable crystalline compounds which can readily be prepared by treating any water-soluble Pb^{II} salt with HX or halide ions to precipitate the insoluble PbX_2 . As with Sn , the first two ionization energies of Pb are very similar to those of Mg ; moreover, the 6-coordinate radius of Pb^{II} (119 pm) is virtually identical with that of Sr^{II} (118 pm) and there is less evidence of the structurally distorting influence of the nonbonding pair of electrons. Thus α - PbF_2 , PbCl_2 , and PbBr_2 all form colourless orthorhombic crystals in which Pb^{II} is surrounded by 9 X at the corners of a tricapped trigonal prism. There are, in fact, never 9 equidistant X neighbours but a range of distances in which one can discern 7 closer and 2 more distant neighbours. This (7 + 2)-coordination is also a feature of the structures of BaX_2 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$), EuCl_2 , CaH_2 , etc.; see also hydrated tin(II) bromides, p. 380.

The high-temperature β -form of PbF_2 has the cubic fluorite (CaF_2) structure with 8-coordinated Pb^{II} . PbI_2 (yellow) has the CdI_2 hexagonal layer lattice structure. Like many other heavy-metal halides, PbCl_2 and PbBr_2 are photo-sensitive and deposit metallic Pb on irradiation with ultraviolet or visible light. PbI_2 is a photoconductor and decomposes on exposure to green light ($\lambda_{\text{max}} 494.9 \text{ nm}$). Many mixed halides have also been characterized, e.g. PbFCl , PbFBr , PbFI , $\text{PbX}_2 \cdot 4\text{PbF}_2$, etc. Of these PbFCl is an important tetragonal layer-lattice structure type frequently adopted by large cations in the presence of 2 anions of differing size;⁽³⁸⁾ its sparing solubility in water (37 mg per 100 cm^3 at 25°C) forms the basis of a gravimetric method of determining F. It is also interesting to note that PbF_2 was the first ionically conducting crystalline compound to be discovered (Michael Faraday, 1838).

Property	PbF_2	PbCl_2
MP/ $^\circ\text{C}$	818	500
BP/ $^\circ\text{C}$	1290	953
Density/ g cm^{-3}	8.24 (α), 7.77 (β)	5.85
Solubility in		
H_2O ($T^\circ\text{C}$)/	64 (20°)	670 (0°)
mg per 100 cm^3		3200 (100°)
Property	PbBr_2	PbI_2
MP/ $^\circ\text{C}$	367	400
BP/ $^\circ\text{C}$	916	860–950 (decomp)
Density/ g cm^{-3}	6.66	6.2
Solubility in		
H_2O ($T^\circ\text{C}$)/	455 (0°)	44 (0°)
mg per 100 cm^3	4710 (100°)	410 (100°)

Pb^{II} apparently forms complexes with an astonishing range of stoichiometries,⁽³⁹⁾ but structural information is frequently lacking. Cs_4PbX_6 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) have the K_4CdCl_6 structure with discrete $[\text{Pb}^{\text{II}}\text{X}_6]^{4-}$ units. $\text{CsPb}^{\text{II}}\text{X}_3$ also feature octahedral coordination (in perovskite-like structures, cf. p. 963) but there is sometimes appreciable distortion as in the yellow, low-temperature form of CsPbI_3 which adopts the NH_4CdCl_3 structure with three Pb – I distances, 301, 325, and 342 pm. Note also the orange-yellow crystalline compound of overall composition $[\text{Co}(\text{en})_3\text{PbCl}_5 \cdot 1.5\text{H}_2\text{O}]$ which in fact features a novel chain anion $[\text{Pb}_2\text{Cl}_9]_n^{5n-}$ and should be formulated $[\text{Co}(\text{en})_3]_2[\text{Pb}_2\text{Cl}_9]\text{Cl} \cdot 3\text{H}_2\text{O}$.⁽⁴⁰⁾ There are also many ternary solid state compounds, e.g. $\text{Pb}_{13}^{\text{II}}\text{O}_{10}\text{Br}_6$.⁽⁴¹⁾

10.3.3 Oxides and hydroxides

GeO is obtained as a yellow sublimate when powdered Ge and GeO_2 are heated to 1000° , and dark-brown crystalline GeO is obtained on further heating at 650° . The compound can also be obtained by dehydrating $\text{Ge}(\text{OH})_2$

³⁹ E. W. ABEL, Lead, Chap. 18 in *Comprehensive Inorganic Chemistry*, Vol. 2, pp. 105–46, Pergamon Press, Oxford, 1973.

⁴⁰ A. AQUILINO, M. CANNAS, A. CHRISTINI and G. MARONGIU, *J. Chem. Soc., Chem. Commun.*, 347–8 (1978).

⁴¹ H.-J. RIEBE and H.-L. KELLER, *Z. anorg. allg. Chem.* **571**, 139–47 (1989).

³⁸ N. N. GREENWOOD, *Ionic Crystals, Lattice Defects, and Nonstoichiometry*, pp. 59–60, Butterworths, London 1968.

(p. 376) but neither compound is particularly well characterized. Both are reducing agents and GeO disproportionates rapidly to Ge and GeO₂ above 700°. Much more is known about GeO₂ and there is an impressive resemblance between the oxide chemistry of Ge^{IV} and Si^{IV}. Thus hexagonal GeO₂ has the 4-coordinated β -quartz structure (p. 342), tetragonal GeO₂ has the 6-coordinated rutile-like structure of stishovite (p. 343), and vitreous GeO₂ resembles fused silica. Similarly, Ge analogues of all the major types of silicates and aluminosilicates (pp. 347–59) have been prepared. Be₂GeO₄ and Zn₂GeO₄ have the phenacite and willemite structures with “isolated” {GeO₄} units; Sc₂Ge₂O₇ has the thortveitite structure; BaTiGe₃O₉ has the same type of cyclic ion as benitoite, and CaMgGe₂O₆ has a chain structure similar to diopside. Further, the two crystalline forms of Ca₂GeO₄ are isostructural with two forms of Ca₂SiO₄, and Ca₃GeO₅ crystallizes in no fewer than 4 of the known structures of Ca₃SiO₅. The reaction chemistry of the two sets of compounds is also very similar.

SnO exists in several modifications. The commonest is the blue-black tetragonal modification formed by the alkaline hydrolysis of Sn^{II} salts to the hydrous oxide and subsequent dehydration in the absence of air. The structure features square

pyramids of {SnO₄} arranged in parallel layers with Sn^{II} at the apex and alternately above and below the layer of O atoms as shown in Fig. 10.6. The Sn–Sn distance between tin atoms in adjacent layers is 370 pm, very close to the values in β -Sn (p. 372). The structure can also be described as a fluorite lattice with alternate layers of anions missing. A metastable, red modification of SnO is obtained by heating the white hydrous oxide; this appears to have a similar structure and it can be transformed into the blue-black form by heating, by pressure, by treatment with strong alkali or simply by contact with the stable form. Both forms oxidize to SnO₂ with incandescence when heated in air to ~300° but when heated in the absence of O₂, the compound disproportionates like GeO. Various mixed-valence oxides have also been reported of which the best characterized is Sn₃O₄, i.e. Sn^{II}Sn^{IV}O₄.

SnO and hydrous tin(II) oxide are amphoteric, dissolving readily in aqueous acids to give Sn^{II} or its complexes, and in alkalis to give the pyramidal Sn(OH)₃⁻; at intermediate values of pH, condensed basic oxide–hydroxide species form, e.g. [(OH)₂SnOSn(OH)₂]²⁻ and [Sn₃(OH)₄]²⁺, etc. Analytically, the hydrous oxide frequently has a composition close to 3SnO·H₂O and an X-ray study shows it to

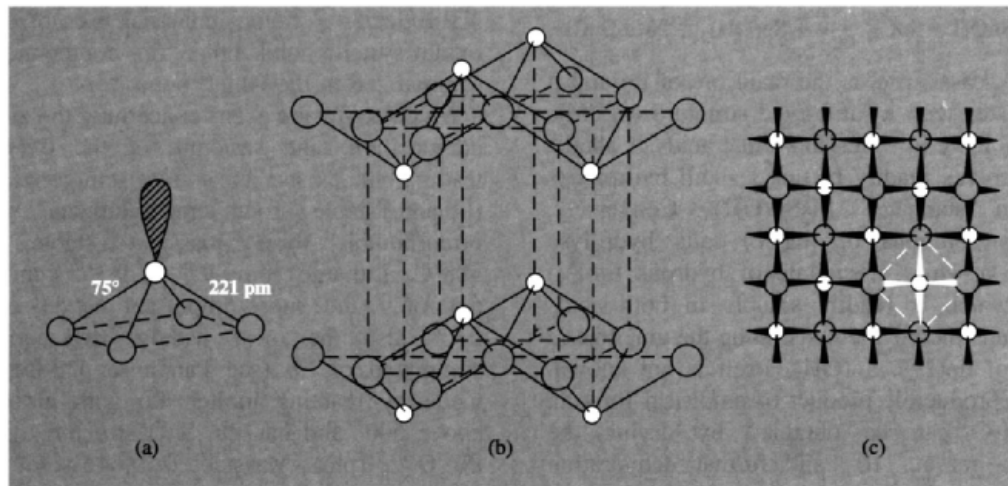
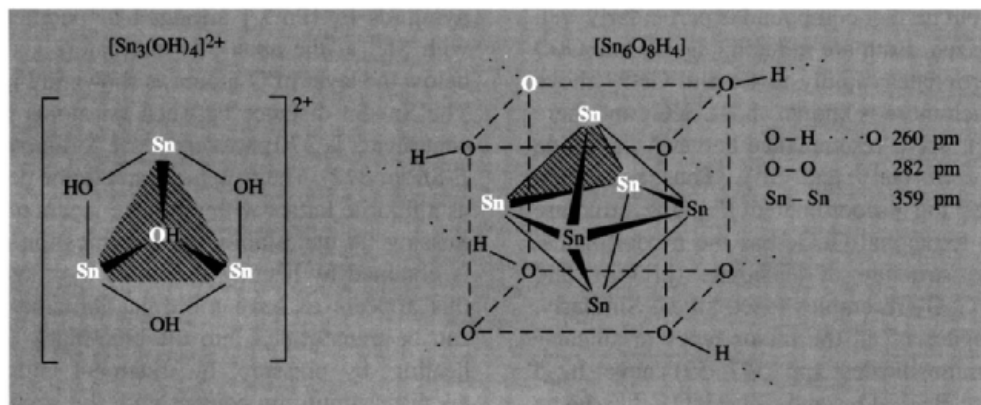
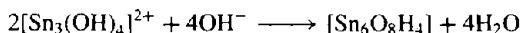


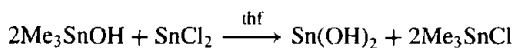
Figure 10.6 Structure of tetragonal SnO (and PbO) showing (a) a single square-based pyramid {SnO₄}, (b) the arrangement of the pyramids in layers, and (c) a plane view of a single layer.



contain pseudo-cubic Sn₆O₈ clusters resembling Mo₆Cl₈⁴⁺ (p. 1022) with 8 oxygen atoms centred above the faces of an Sn₆ octahedron and joined in infinite array by H bonds, i.e. Sn₆O₈H₄; the compound can be thought of as being formed by the deprotonation and condensation of 2[Sn₃(OH)₄]²⁺ units as the pH is raised:



(Hydrolysis of Pb^{II} salts leads to different structures, p. 395.) It seems unlikely that pure Sn(OH)₂ itself has ever been prepared from aqueous solutions but it can be obtained as a white, amorphous solid by an anhydrous organometallic method:⁽⁴²⁾



SnO₂, cassiterite, is the main ore of tin and it crystallizes with a rutile-type structure (p. 961): It is insoluble in water and dilute acids or alkalis but dissolves readily in fused alkali hydroxides to form "stannates" M₂Sn(OH)₆. Conversely, aqueous solutions of tin(IV) salts hydrolyse to give a white precipitate of hydrous tin(IV) oxide which is readily soluble in both acids and alkalis thereby demonstrating the amphoteric nature of tin(IV). Sn(OH)₄ itself is not known, but a reproducible product of empirical formula SnO₂·H₂O can be obtained by drying the hydrous gel at 110°, and further dehydration

at temperatures up to 600° eventually yields crystalline SnO₂. Similarly, thermal dehydration of K₂[Sn(OH)₆], i.e. "K₂SnO₃·3H₂O", yields successively K₂SnO₃·H₂O, 3K₂SnO₃·2H₂O and, finally, anhydrous K₂SnO₃; this latter compound also results when K₂O is heated directly with SnO₂, and variations in the ratio of the two reactants yield K₄SnO₄ and K₂Sn₃O₇. The structure of K₂SnO₃ does not have 6-coordinate Sn^{IV} but chains of 5-coordinate Sn^{IV} of composition {SnO₃} formed by the edge sharing of tetragonal pyramids of {SnO₅} as shown in Fig. 10.7. The colourless compound RbNa₃SnO₄, formed by heating RbSn and Na₂O₂ at 750° has tetrahedral SnO₄⁴⁻ units (Sn-O 196 pm); it is isotypic with NaLi₃SiO₄ and NaLi₃GeO₄.⁽⁴³⁾ Some industrial uses of tin(IV) oxide systems and other tin compounds are summarized in the Panel (opposite).

Much confusion exists concerning the number, composition, and structure of the oxides of lead. PbO exists as a red tetragonal form (litharge) stable at room temperature and a yellow orthorhombic form (massicot) stable above 488°C. Litharge (mp 897°, *d* 9.355 g cm⁻³) is not only the most important oxide of Pb, it is also the most widely used inorganic compound of Pb (see Panel on p. 386); it is made by reacting molten Pb with air or O₂ above 600° and has the SnO structure (p. 383, Pb-O 230 pm). Massicot (*d* 9.642 g cm⁻³) has

⁴² W. D. HONNICK and J. J. ZUCKERMAN, *Inorg. Chem.* **15**, 3034-7 (1976).

⁴³ K. BERNET and R. HOPPE, *Z. anorg. allg. Chem.* **571**, 101-12 (1989).

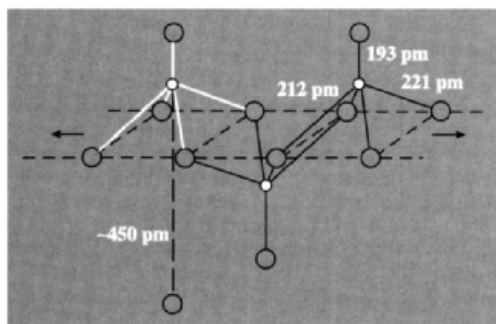


Figure 10.7 $\{\text{SnO}_3\}$ chain in the structure of K_2SnO_3 (and K_2PbO_3).

a distorted version of the same structure. The mixed-valency oxide Pb_3O_4 (red lead, minium, d 8.924 g cm^{-3}) is made by heating PbO in air in a reverberatory furnace at $450\text{--}500^\circ$ and is important commercially as a pigment and primer (see Panel on p. 386). Its structure (Fig. 10.8) consists of chains of $\text{Pb}^{\text{IV}}\text{O}_6$ octahedra ($\text{Pb}\text{--O}$

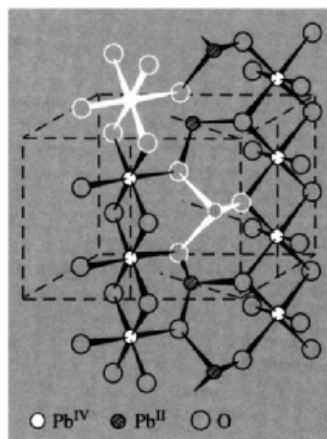


Figure 10.8 Portion of the crystal structure of Pb_3O_4 showing chains of edge-shared $\text{Pb}^{\text{IV}}\text{O}_6$ octahedra joined by pyramids of $\text{Pb}^{\text{II}}\text{O}_3$; the mean $\text{O}\text{--Pb}^{\text{II}}\text{--O}$ angle is 76° as in PbO .

214 pm) sharing opposite edges, these chains being linked by the Pb^{II} atoms which themselves

Some Industrial Uses of Tin Compounds

Tin(IV) oxide is much used in the ceramics industry as an opacifier for glazes and enamels. Because of its insolubility (or, rather, slow solubility) in glasses and glazes it also serves as a base for pigments, e.g. $\text{SnO}_2/\text{V}_2\text{O}_5$ yellows, $\text{SnO}_2/\text{Sb}_2\text{O}_5$ blue-greys and $\text{SnO}_2/\text{Cr}_2\text{O}_3$ pinks. These latter, which can vary from a delicate pale pink to a dark maroon, probably involve substitutional incorporation of Cr^{III} for Sn^{IV} with concomitant oxide-ion vacancies, i.e. $[\text{Sn}^{\text{IV}}_{1-2x}\text{Cr}^{\text{III}}_x\text{O}_{2-x}^{\text{II}}] (\square^-)_x$. The vanadium- and antimony-tin glazes, on the other hand, probably involve reductive substitution without vacant sites, e.g. $[\text{Sn}^{\text{IV}}_{1-3x}\text{Sn}^{\text{II}}\text{Sb}_x\text{O}_{2-x}^{\text{II}}]$. Some 3500 tonnes of SnO_2 are consumed annually for ceramic glazes.

A related application is the use of SnCl_4 vapour to toughen freshly fabricated glass bottles by deposition of an invisible transparent film of SnO_2 ($<0.1 \mu\text{m}$) which is then incorporated in the surface structure of the glass. This increases the strength of the glass and improves its abrasion resistance so that bottles so treated can be made considerably lighter without loss of robustness. When the thickness of the SnO_2 film is similar to the wavelength of visible light ($0.1\text{--}1.0 \mu\text{m}$), then thin-film interference effects occur and the glass acquires an attractive iridescence. Still thicker films give electrically conducting layers which, after suitable doping with Sb or F ions, can be used as electrodes, electro-luminescent devices (for low-intensity light panels and display signs, in aircraft, cinemas, etc.), fluorescent lamps, antistatic cover-glasses, transparent tube burners, deiceable windcreens (especially for aircraft), etc. Another property of these thicker films is their ability to reflect a high proportion of infrared (heat) radiation whilst remaining transparent to visible radiation — the application to heat insulation of windows is obvious.

Attention should be drawn to the use of tin oxide systems as heterogeneous catalysts. The oldest and most extensively patented systems are the mixed tin–vanadium oxide catalysts for the oxidation of aromatic compounds such as benzene, toluene, xylenes and naphthalene in the synthesis of organic acids and acid anhydrides. More recently mixed tin–antimony oxides have been applied to the selective oxidation and ammoxidation of propylene to acrolein, acrylic acid and acrylonitrile.

Homogeneous catalysis by tin compounds is also of great industrial importance. The use of SnCl_4 as a Friedel–Crafts catalyst for homogeneous acylation, alkylation and cyclization reactions has been known for many decades. The most commonly used industrial homogeneous tin catalysts, however, are the Sn(II) salts of organic acids (e.g. acetate, oxalate, oleate, stearate and octoate) for the curing of silicone elastomers and, more importantly, for the production of polyurethane foams. World consumption of tin catalysts for these last applications alone is over 1000 tonnes pa.

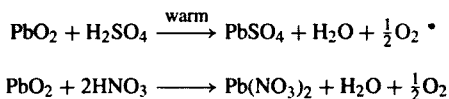
For uses of organotin compounds (i.e. compounds having at least one Sn–C bond), see p. 400.

The Oxides of Lead^(9,10)

PbO (red, orange or yellow depending on the method of preparation) is amphoteric and dissolves readily in both acids and alkalis. It is much used in glass manufacture since a high Pb content leads to greater density, lower thermal conductivity, higher refractive index (greater brilliance), and greater stability and toughness. The replacement of the very mobile alkali ions by Pb also leads to high electrical capacities, comparable with mica. PbO is also used to form stable ceramic glazes and vitreous enamels (see SnO₂, p. 385). Electric storage batteries are the other major user of PbO (either as litharge or as "black oxide", i.e. PbO + Pb). The plates of the battery consist of an inactive grid or support onto which is applied a paste of PbO/H₂SO₄. The positive plates are activated by oxidizing PbO to PbO₂ and the negative plates by reducing PbO to Pb. Another use of PbO is in the production of pigments (p. 371).

Red lead (Pb₃O₄) is manufactured on the 20000-tonne scale annually and is used primarily as a surface coating to prevent corrosion of iron and steel (check oxidation-reduction potentials). It is also used in the production of leaded glasses and ceramic glazes and, very substantially, as an activator, vulcanizing agent and pigment in natural and artificial rubbers and plastics.

PbO₂ is a strong oxidizing agent and, in addition to its *in situ* production in storage batteries, it is independently manufactured for use as an oxidant in the manufacture of chemicals, dyes, matches and pyrotechnics. It is also used in considerable quantity as a curing agent for sulfide polymers and in high-voltage lightning arresters. Because of the instability of Pb^{IV}, PbO₂ tends to give salts of Pb^{II} with liberation of O₂ when treated with acids, e.g.

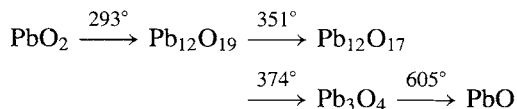


Warm HCl reacts similarly but in the cold PbCl₄ is obtained. PbO₂ is produced commercially by the oxidation of Pb₃O₄ in alkaline slurry with Cl₂ and the technical product is marketed in 90-kg drums.

Mixed oxides of Pb^{IV} with other metals find numerous applications in technology and industry. They are usually made by heating PbO₂ (or PbO) in air with the appropriate oxide, hydroxide or oxoacid salt, the product formed being dependent on the stoichiometry used, e.g. M^{II}Pb^{IV}O₃, M^{II}Pb^{IV}O₄ (M^{II} = Ca, Sr, Ba). CaPbO₃ in particular is increasingly replacing Pb₃O₄ as a priming pigment to protect steel against corrosion by salt water. Mixed oxides of Pb^{II} are also important. Ferrimagnetic oxides of general formula PbO.*n*Fe₂O₃ (*n* = 6, 5, 2.5, 1, 0.5) can be prepared by direct reaction but have not proved to be as attractive, commercially, as the hard ferrite BaFe₁₂O₁₉. By contrast, the ferroelectric behaviour (p. 57) of several mixed oxides with Pb^{II} has excited considerable interest. Many of these compounds have a distorted perovskite-type structure (p. 963); e.g. yellow PbTiO₃ (ferroelectric below 490°C), colourless PbZrO₃ (230°), and PbHfO₃ (215°, antiferroelectric). Others have a tetragonal tungsten-bronze-type structure (p. 1016), e.g. PbNb₂O₆ (ferroelectric up to 560°C), PbTi₂O₆ (~215°). The mode of action and uses of hard ferroelectrics has been discussed on p. 58, and the high Curie temperature of many Pb^{II} ferroelectrics makes them particularly useful for high-temperature applications.

are pyramidally coordinated by 3 oxygen atoms (2 at 218 pm and 1 at 213 pm). The dioxide normally occurs as the maroon-coloured PbO₂(I) which has the tetragonal, rutile structure (Pb^{IV}-O 218 pm, *d* 9.643 g cm⁻³), but there is also a high-pressure, black, orthorhombic polymorph, PbO₂(II) (*d* 9.773 g cm⁻³).

When PbO₂ is heated in air it decomposes as follows:⁽⁴⁴⁾



In addition, a sesquioxide Pb₂O₃ can be obtained as vitreous black monoclinic crystals (*d* 10.046 g cm⁻³) by decomposing PbO₂ (or PbO) at 580–620° under an oxygen pressure of 1.4 kbar: in this compound the Pb^{II} atoms are situated between layers of distorted Pb^{IV}O₆ octahedra (mean Pb^{IV}-O 218 pm) with 3 Pb^{II}-O in the range 231–246 pm and 3 in the range 264–300 pm. The monoclinic compound Pb₁₂O₁₉ (i.e. PbO_{1.583}) forms dark-brown or black crystals which have a pseudocubic defect-fluorite structure with 10 ordered anion vacancies according to the formulation [Pb₂₄O₃₈(□₋)₁₀] and no detectable variability of composition. It will be recalled that PbO can be considered as a defect fluorite structure in which each alternate layer

⁴⁴ W. B. WHITE and R. RAY, *J. Am. Ceram. Soc.* **47**, 242–7 (1964) and references therein.

of O atoms in the (001) direction is missing (p. 383), i.e. $[\text{Pb}_{24}\text{O}_{24}(\square)_{24}]$; it therefore seems reasonable to suppose that the anion vacancies in $[\text{Pb}_{24}\text{O}_{38}(\square)_{10}]$ are also confined to alternate layers, though it is not clear why this structure should show no variability in composition. Further heating above 350° (or careful oxidation of PbO) yields $\text{Pb}_{12}\text{O}_{17}$ (i.e. $\text{PbO}_{1.417}$) which is also a stoichiometric ordered defect fluorite structure $[\text{Pb}_{24}\text{O}_{34}(\square)_{14}]$. However, oxidation of this phase under increasing oxygen pressure leads to a nonstoichiometric phase of variable composition between $\text{PbO}_{1.42}$ and $\text{PbO}_{1.57}$ in which there appears to be a quasi-random array of anion vacancies.⁽⁴⁵⁾

Lead does not appear to form a simple hydroxide, $\text{Pb}(\text{OH})_2$, [cf. $\text{Sn}(\text{OH})_2$, p. 384]. Instead, increasing the pH of solutions of Pb^{II} salts leads to hydrolysis and condensation, see $[\text{Pb}_6\text{O}(\text{OH})_6]^{4+}$ (p. 395).

10.3.4 Derivatives of oxoacids

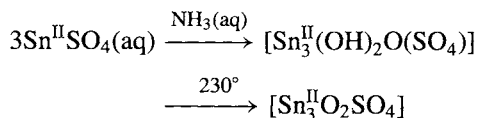
Oxoacid salts of Ge are usually unstable, generally uninteresting, and commercially unimportant. The tetraacetate $\text{Ge}(\text{OAc})_4$ separates as white needles, mp 156° , when GeCl_4 is treated with TIOAc in acetic anhydride and the resulting solution is concentrated at low pressure and cooled. An unstable sulfate $\text{Ge}(\text{SO}_4)_2$ is formed in a curious reaction when GeCl_4 is heated with SO_3 in a sealed tube at 160° :



Numerous oxoacid salts of Sn^{II} and Sn^{IV} have been reported and several basic salts are also known. Anhydrous $\text{Sn}(\text{NO}_3)_2$ has not been prepared but the basic salt $\text{Sn}_3(\text{OH})_4(\text{NO}_3)_2$ can be made by reacting a paste of hydrous tin(II) oxide with aqueous HNO_3 ; the compound may well contain the oligomeric cation $[\text{Sn}_3(\text{OH})_4]^{2+}$ illustrated on p. 384. $\text{Sn}(\text{NO}_3)_4$ can be obtained in anhydrous reactions of

SnCl_4 with N_2O_5 , ClNO_3 or BrNO_3 ; the compound readily oxidizes or nitrates organic compounds, probably by releasing reactive NO_3 radicals. Many phosphates and phosphato complexes have been described: typical examples for Sn^{II} are $\text{Sn}_3(\text{PO}_4)_2$, SnHPO_4 , $\text{Sn}(\text{H}_2\text{PO}_4)_2$, $\text{Sn}_2\text{P}_2\text{O}_7$ and $\text{Sn}(\text{PO}_3)_2$. Examples with Sn^{IV} are $\text{Sn}_2\text{O}(\text{PO}_4)_2$, $\text{Sn}_2\text{O}(\text{PO}_4)_2 \cdot 10\text{H}_2\text{O}$, SnP_4O_7 , $\text{KSn}(\text{PO}_4)_3$, KSnOPO_4 and $\text{Na}_2\text{Sn}(\text{PO}_4)_2$. One remarkable compound is tin(IV) hypophosphite, $\text{Sn}(\text{H}_2\text{PO}_2)_4$ since it contains Sn^{IV} in the presence of the strongly reducing hypophosphorous anion; it has been suggested that the isolation of $\text{Sn}(\text{H}_2\text{PO}_2)_4$ (colourless crystals) by bubbling O_2 through a solution of SnO in hypophosphorous acid, $[\text{H}_2\text{PO}(\text{OH})]$, may be due to a combination of kinetic effects and the low solubility of the product.

Treatment of SnO_2 with hot dilute H_2SO_4 yields the hygroscopic dihydrate $\text{Sn}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$. In the Sn^{II} series SnSO_4 is a stable, colourless compound which is probably the most convenient laboratory source of Sn^{II} uncontaminated with Sn^{IV} ; it is readily prepared by using metallic Sn to displace Cu from aqueous solutions of CuSO_4 . SnSO_4 was at one time thought to be isostructural with BaSO_4 but this seemed unlikely in view of the very different sizes of the cations and the known propensity of Sn^{II} to form distorted structures; it is now known to consist of $\{\text{SO}_4\}$ groups linked into a framework by O–Sn–O bonds in such a way that Sn is pyramidally coordinated by 3 O atoms at 226 pm (O–Sn–O angles 77 – 79°); other Sn–O distances are much larger and fall in the range 295–334 pm.⁽⁴⁶⁾ A basic sulfate and oxosulfate are also known:



The crystal structures of the oxalates SnC_2O_4 and $\text{K}_2\text{Sn}(\text{C}_2\text{O}_4)_2 \cdot \text{H}_2\text{O}$ show interesting features⁽⁴⁷⁾

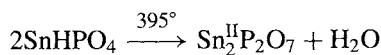
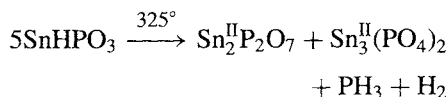
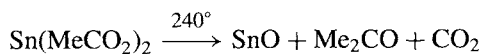
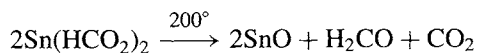
⁴⁶ J. D. DONALDSON and D. C. PUXLEY, *Acta Cryst.* **28B**, 864–7 (1972).

⁴⁷ A. D. CHRISTIE, R. A. HOWIE and W. MOSER, *Inorg. Chim. Acta.* **36**, L447–L448 (1979).

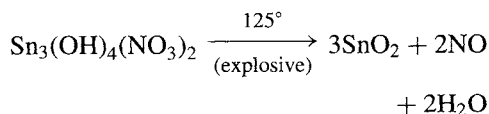
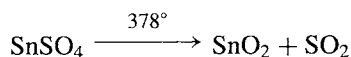
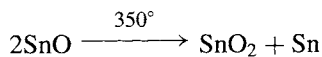
⁴⁵ J. S. ANDERSON and M. STERNS, *J. Inorg. Nucl. Chem.* **11**, 272–85 (1959).

reminiscent of tetragonal SnO (Fig. 10.6). The organotin(IV) sulfate $(\text{Me}_3\text{Sn})_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ has trigonal bipyramidal Sn with *trans*- O_2SnMe_3 stereochemistry, i.e. $[\text{H}_2\text{O}-\text{SnMe}_3-(\mu-\text{OSO}_2\text{O})-\text{SnMe}_3-\text{OH}_2]$; H-bonding between the two non-bridging O-atoms of the sulfate group and water molecules in neighbouring units produces a three-dimensional network.⁽⁴⁸⁾ In general, the product obtained by the thermal decomposition of Sn^{II} oxoacid salts depends on the coordinating strength of the oxoacid anion. For strong ligands such as formate, acetate and phosphite, other Sn^{II} compounds are formed (often SnO), whereas for less-strongly coordinating ligands such as the sulfate or nitrate internal oxidation to SnO_2 occurs, e.g.:

Strong ligands:



Weak ligands:



Most oxoacid derivatives of lead are Pb^{II} compounds, though $\text{Pb}(\text{OAc})_4$ is well known and is extensively used as a selective oxidizing agent in organic chemistry.⁽⁴⁹⁾ It can be obtained as

colourless, moisture-sensitive crystals by treating Pb_3O_4 with glacial acetic acid. $\text{Pb}(\text{SO}_4)_2$ is also stable when dry and can be made by the action of conc H_2SO_4 on $\text{Pb}(\text{OAc})_4$ or by electrolysis of strong H_2SO_4 between Pb electrodes. PbSO_4 is familiar as a precipitate for the gravimetric determination of sulfate (solubility 4.25 mg per 100 cm³ at 25°C); PbSeO_4 is likewise insoluble. By contrast $\text{Pb}(\text{NO}_3)_2$ is very soluble in water (37.7 g per 100 cm³ at 0°, 127 g at 100°). The diacetate is similarly soluble (19.7 and 221 g per 100 cm³ at 0° and 50° respectively). Both compounds find wide use in the preparation of Pb chemicals by wet methods and are made simply by dissolving PbO in the appropriate aqueous acid. A large number of basic nitrates and acetates is also known. The thermal decomposition of anhydrous $\text{Pb}(\text{NO}_3)_2$ above 400° affords a convenient source of N_2O_4 (see p. 456).

Other important Pb^{II} salts are the carbonate, basic carbonate, silicates, phosphates and perchlorate, but little new chemistry is involved. PbCO_3 occurs as cerussite; the compound is made as a dense white precipitate by treating the nitrate or acetate with CO_2 in the presence of $(\text{NH}_4)_2\text{CO}_3$ or Na_2CO_3 , care being taken to keep the temperature low to avoid formation of the basic carbonate $\sim 2\text{Pb}(\text{CO}_3) \cdot \text{Pb}(\text{OH})_2$. These compounds were formerly much used as pigments (white lead) but are now largely replaced by other white pigments such as TiO_2 which has higher covering power and lower toxicity. The highly soluble perchlorate [and even more the tetrafluoroborate $\text{Pb}(\text{BF}_4)_2$] are much used as electrolytic plating baths for the deposition of Pb to impart corrosion resistance or lubricating properties to various metal parts. Throughout the chemistry of the oxoacid salts of Pb^{II} the close correlation between anionic charge and aqueous solubility is apparent.

The complex coordination chemistry of Pb^{II} is also beginning to be actively explored and some unusual stereochemistries are emerging. Thus, the mononuclear $(\eta^2\text{-nitrato})\text{bis}(\text{phenanthroline})(N\text{-thiocyanato})$ complex $[\text{Pb}(\text{phen})_2(\text{NCS})(\eta^2\text{-NO}_3)]$ has 7-coordinate Pb^{II} with a large vacancy

⁴⁸ K. C. MOLLOY, K. QUILL, D. CUNNINGHAM, P. MCARDLE and T. HIGGINS, *J. Chem. Soc., Dalton Trans.*, 267–73 (1989).

⁴⁹ R. N. BUTLER, in J. S. PIZEY (ed.), *Synthetic Reagents*, Vol. 3, pp. 278–419, Wiley Chichester, 1977.