compounds such as $[PhAs(Cr(CO)_5)_2]$ and $[PhSb(Mn(\eta^5\text{-}C_5H_5)(CO)_2)_2]$ (p. 597) See later, also, for examples of CN 4 (tetrahedral, flattened tetrahedral and see-saw), CN 5 (trigonal bipyramidal and square pyramidal) and CN 6 (octahedral, 3 + 3, and pentagonal pyramidal).

Higher coordination numbers are less common and are mainly confined to Bi. CN 7 has been found in the tetradendate crown-ether bismuth complex $[BiCl_3(12\text{-crown-4})]^{(10)}$ and in the bismuth complex, [BiL], of the novel heptadentate anionic ligand of 'saltren', (H_3L), i.e. $(N(CH_2CH_2N{=}CHC_6H_4OH)_3)$.[11] The first example of CN 8 was found in the colourless 2:1 adduct $[2BiCl_3.18\text{-crown-6}]$ which was shown by X-ray analysis to involve an unexpected ionic structure featuring 8-coordinate Bi cations, viz. $[BiCl_2(18\text{-crown-6})]^+{}_2[Bi_2Cl_8]^{2-}$.[10] CN 9 is represented by the discrete tris(tridentate) complex $[Bi(-O-C(Bu^t){=}C-N{=}C-C(Bu^t){=}O{\rightarrow})_3]$ in which Bi has a face-capped, slightly-twisted trigonal-prismatic coordination environment.[12] Still higher coordination numbers are exemplified by encapsulated As and Sb atoms in rhodium carbonyl cluster anions: for example As is surrounded by a bicapped square antiprism of 10 Rh atoms in $[Rh_{10}As(CO)_{22}]^{3-}$,[13] and Sb is surrounded by an icosahedron of 12 Rh in $[Rh_{12}Sb(CO)_{27}]^{3-}$.[14] In each case the anion is the first example of a complex in which As or Sb acts as a 5-electron donor (cf. P as a 5-electron donor in $[Rh_9P(CO)_{21}]^{3-}$): all these clusters then have precisely the appropriate number of valence electrons for *closo* structures on the basis of Wade's rules (pp. 161, 174).

13.3 Compounds of Arsenic, Antimony and Bismuth[15]

13.3.1 Intermetallic compounds and alloys[16,17]

Most metals form arsenides, antimonides and bismuthides, and many of these command attention because of their interesting structures or valuable physical properties. Like the borides (p. 145), carbides (p. 297), silicides (p. 335), nitrides (p. 417) and phosphides (p. 489), classification is difficult because of the multitude of stoichiometries, the complexities of the structures and the intermediate nature of the bonding. The compounds are usually prepared by direct reaction of the elements in the required proportions and typical compositions are M_9As, M_5As, M_4As, M_3As, M_5As_2, M_2As, M_5As_3, M_3As_2, M_4As_3, M_5As_4, MAs, M_3As_4, M_2As_3, MAs_2 and M_3As_7. Antimony and bismuth are similar. Many of these intermetallic compounds exist over a range of composition, and nonstoichiometry is rife.

The (electropositive) alkali metals of Group 1 form compounds M_3E (E = As, Sb, Bi) and the metals of Groups 2 and 12 likewise form M_3E_2. These can formally be written as $M^+{}_3E^{3-}$ and $M^{2+}{}_3E^{3-}{}_2$ but the compounds are even less ionic than Li_3N (p. 76) and have many metallic properties. Moreover, other stoichiometries are found (e.g. $LiBi$, KBi_2, $CaBi_3$) which are not readily accounted for by the ionic model and, conversely, compounds M_3E are formed by many metals that are not usually thought of as univalent, e.g. Ti, Zr, Hf; V, Nb, Ta; Mn. There are clearly also strong additional interactions between unlike atoms as indicated by the structures adopted and the high mp of many of the compounds, e.g. Na_3Bi melts

[10] N. W. ALCOCK, M. RAVINDRAN and G. R. WILLEY, *J. Chem. Soc., Chem. Commun.*, 1063–5 (1989).

[11] P. K. BHARADWAJ, A. M. LEE, S. MANDAL, B. W. SKELTON and A. H. WHITE, *Aust. J. Chem.* **47**, 1799–803 (1994).

[12] C. A. STEWART, J. C. CALABRESE and A. J. ARDUENGO, *J. Am. Chem. Soc.* **107**, 3397–8 (1985).

[13] J. L. VIDAL *Inorg. Chem.* **20**, 243–9 (1981).

[14] J. L. VIDAL and J. M. TROUP, *J. Organometallic Chem.* **213**, 351–63 (1981).

[15] C. A. MCAULIFFE and A. G. MACKIE *Chemistry of Arsenic, Antimony and Bismuth*, Ellis Horwood, Chichester, 1990, 350 pp.

[16] J. D. SMITH, Chap. 21 in *Comprehensive Inorganic Chemistry*, Vol. 2, pp. 547–683, Pergamon Press, Oxford, 1973.

[17] F. HULLIGER, *Struct. Bond.* **4**, 83–229 (1968). A comprehensive review with 532 references.

at 840°, compared with Na 98° and Bi 271°C. Many of the M_3E compounds have the hexagonal Na_3As (anti-LaF_3) structure in which equal numbers of Na and As form hexagonal nets as in boron nitride and the remaining Na atoms are arranged in layers on either side of these nets. Each As has 5 Na neighbours at the corners of a trigonal bipyramid (3 at 294 and 2 at 299) and 6 other Na atoms at 330 pm form a trigonal prism (i.e. 11-coordinate). The Na atoms are of two sorts, both of high mixed CN to As and Na, and all the Na–Na distances (328–330 pm) are less than in Na metal (371.6 pm). The compounds show either metallic conductivity or are semiconductors. An even more compact metal structure (cubic) is adopted by β-Li_3Bi, β-Li_3Sb, and by M_3E, where M = Rb, Cs, and E = Sb, Bi.

Some of the alkali metal–group 15 element systems give compounds of stoichiometry ME. Of these, LiBi and NaBi have typical alloy structures and are superconductors below 2.47 K and 2.22 K respectively. Others, like LiAs, NaSb and KSb, have parallel infinite spirals of As or Sb atoms, and it is tempting to formulate them as $M^+{}_n(E_n)^{n-}$ in which the $(E_n)^{n-}$ spirals are isoelectronic with those of covalently catenated Se and Te (p. 752); however, their metallic lustre and electrical conductivity indicate at least some metallic bonding. Within the spiral chains As–As is 246 pm (cf. 252 pm in the element) and Sb–Sb is ~285 pm (cf. 291 pm in the element).

Compounds with Sc, Y, lanthanoids and actinoids are of three types. Those with composition ME have the (6-coordinated) NaCl structure, whereas M_3E_4 (and sometimes M_4E_3) adopt the body-centred thorium phosphide structure (Th_3P_4) with 8-coordinated M, and ME_2 are like $ThAs_2$ in which each Th has 9 As neighbours. Most of these compounds are metallic and those of uranium are magnetically ordered. Full details of the structures and properties of the several hundred other transition metal–Group 15 element compounds fall outside the scope of this treatment, but three particularly important structure types should be mentioned because of their widespread occurrence and relation to other structure types, namely $CoAs_3$,

NiAs and structures related to those adopted by FeS_2 (marcasite, pyrites, loellingite, etc.).

$CoAs_3$ occurs in the mineral skutterudite; it is a diamagnetic semiconductor and has a cubic structure related to that of ReO_3 (p. 1047) but with a systematic distortion which results in the generation of well-defined *planar* rings of As_4. The same structure motif is found in MP_3 (M = Co, Ni, Rh, Pd), MAs_3 (M = Co, Rh, Ir) and MSb_3 (M = Co, Rh, Ir). The unit cell (Fig. 13.2) contains 8Co and 24As (i.e. $6As_4$), and it follows from the directions in which the various sets of atoms move, that 2 of the 8 original ReO_3 cells do not contain an As_4 group. Each As has a nearly regular tetrahedral arrangement of 2 Co and 2 As neighbours and each Co has a slightly distorted octahedral coordination group of 6 As. The planar As_4 groups are not quite square, the sides of the rectangle being 246 and 257 pm (cf. 244 pm in the tetrahedral As_4 molecule). The distortions from the ReO_3 structure (in which each As would have had 8 equidistant neighbours at about 330 pm) thus permit the closer approach of the As atoms in groups of 4 though this does not proceed so far as to form 6 equidistant As–As links as in the tetrahedral As_4 molecule. The P–P distances in the P_4 rectangles of the isostructural phosphides are 223 and 231 pm (cf. 225 pm in the tetrahedral P_4 molecule).

The NiAs structure is one of the commonest MX structure types, the number of compounds adopting it being exceeded only by those with the NaCl structure. It is peculiar to compounds formed by the transition elements with either As, Sb, Bi, the chalcogens (p. 748) or occasionally Sn. Examples with the Group 15 elements are Ti(As, Sb), V(P, Sb), CrSb, Mn(As, Sb, Bi), FeSb, Co(As, Sb), Ni(As, Sb, Bi), RhBi, Ir(Sb, Bi), PdSb, Pt(Sb, Bi). The structure is illustrated in Fig. 13.3a: each Ni is 8-coordinate, being surrounded by 6 As and by 2 Ni (which are coplanar with 4 of the As); the As atoms form a hcp lattice in which the interstices are occupied by Ni atoms in such a way that each As is surrounded by a trigonal prism of 6 Ni. Another important feature of the NiAs structure is the close approach of Ni atoms

(a)

(b)

(c)
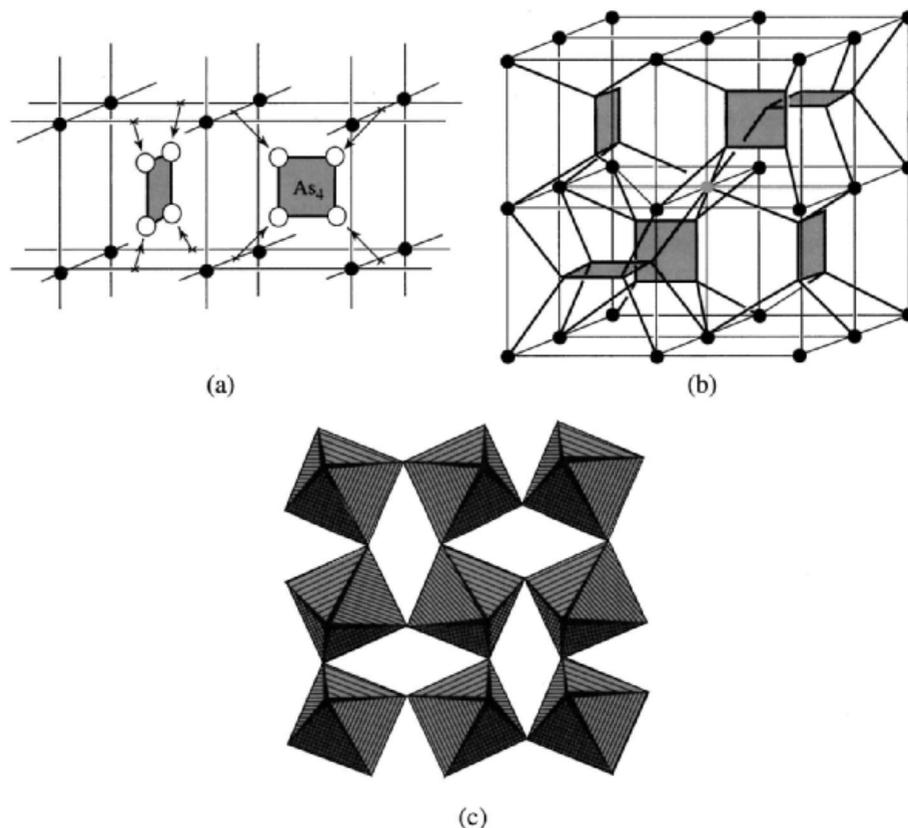
Figure 13.2 The cubic structure of skutterudite ($CoAs_3$). (a) Relation to the ReO_3 structure; (b) unit cell (only sufficient Co–As bonds are drawn to show that there is a square group of As atoms in only 6 of the 8 octants of the cubic unit cell, the complete 6-coordination group of Co is shown only for the atom at the body-centre of the cell); and (c) section of the unit cell showing {$CoAs_6$} octahedra corner-linked to form As_4 squares.

● Ni   (a)

○ As

● Ni   (b)

○ As

● Cd   (c)

○ I
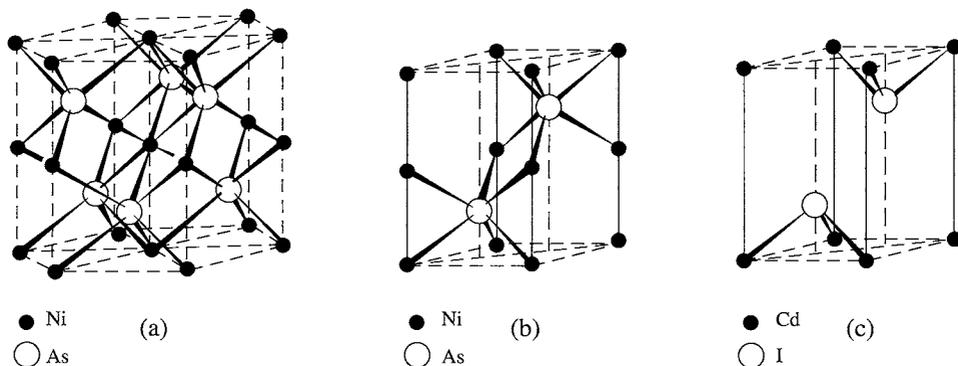
Figure 13.3 Structure of nickel arsenide showing (a) 3 unit cells, (b) a single unit cell Ni_2As_2 and its relation to (c) the unit cell of the layer lattice compound CdI_2 (see text).

in chains along the (vertical) c-axis. The unit cell (Fig. 13.3b) contains Ni_2As_2, and if the central layer of Ni atoms is omitted the CdI_2 structure is obtained (Fig. 13.3c). This structural relationship accounts for the extensive ranges of composition frequently observed in compounds with this structure, since partial filling of the intermediate layer gives compositions in the range $M_{1+x}X_2$ ($0 < x < 1$). With the chalcogens the range sometimes extends the whole way from ME to ME_2 but for As, Sb and Bi it never reaches ME_2 and intermetallic compounds of this composition usually have either the marcasite or pyrites structures of FeS_2 (p. 680) or the compressed marcasite (loellingite) structure of $FeAs_2$. All three structure types contain the E_2 group. Examples are:

marcasite type:	$NiAs_2$, $NiSb_2$
pyrites type:	$PdAs_2$, $PdSb_2$, $PtAs_2$, $PtSb_2$, $PtBi_2$, $AuSb_2$
loellingite type:	$CrSb_2$, FeP_2, $FeAs_2$, $FeSb_2$, RuP_2, $RuAs_2$, $RuSb_2$, OsP_2, $OsAs_2$, $OsSb_2$
ternary compounds:	$CoAsS$ (i.e. "pyrites" $Co_2As_2S_2$), $NiSbS$ {i.e. "pyrites" $Ni(Sb-S)$}, $NiAsS$ (i.e. pyrites with random As and S on the S positions)

Compounds of As, Sb and Bi with the metals in Group 13 (Al, Ga, In, Tl) comprise the important III–V semiconductors whose structures, properties, and extensive applications have already been discussed (pp. 255–8). Group 14 elements also readily form compounds of which the following serve as examples: GeAs mp 737°C, $GeAs_2$ mp 732°C, SnAs

(NaCl structure, superconductor below 3.5 K), Sn_4As_3 (defect NaCl structure, superconductor below 1.2 K). The many important industrial applications of dilute alloys of As, Sb and Bi with tin and lead were mentioned on pp. 370 and 371.

13.3.2 Hydrides of arsenic, antimony and bismuth

AsH_3, SbH_3 and BiH_3 are exceedingly poisonous, thermally unstable, colourless gases whose physical properties are compared with those of NH_3 (p. 423) and PH_3 (p. 492) in Table 13.5. The absence of H bonding is apparent; in addition, the proton affinity is very low and there is little tendency to form the onium ions MH_4^+ analogous to NH_4^+. However, very recently the thermally unstable salts $[AsH_4]^+[SbF_6]^-$ (decomp. $-40°C$), $[AsH_4]^+[AsF_6]^-$ (d. $-75°$) and $[SbH_4]^+[SbF_6]^-$ (d. $-70°$), have been isolated as colourless air- and moisture-sensitive crystals by protonation of the hydrides MH_3 with the appropriate superacids. HF/MF_5 (M = As, Sb).[18] The gradually increasing densities of the liquids near their bp is expected, as is the increase in M–H distance. There is a small diminution in the angle H–M–H with increasing molecular weight though the difference for AsH_3 and SbH_3 is similar to the experimental uncertainty. The rapid diminution in thermal stability is reflected in the standard heats of formation $\Delta H_f°$; AsH_3 decomposes to the elements on being warmed to 250–300°, SbH_3 decomposes steadily
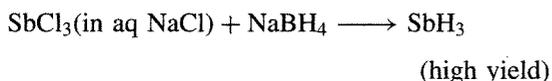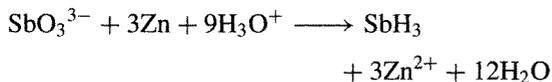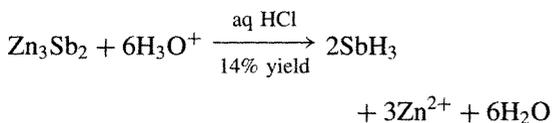
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[18] R. MINKWITZ, A. KORNATH, W. SAWODNY and H. HÄRT-NER, *Z. anorg. allg. Chem.* **620** 753–6 (1994).

Table 13.5   Comparison of the physical properties of AsH_3, SbH_3 and BiH_3 with those of NH_3 and PH_3

| Property	NH_3	PH_3	AsH_3	SbH_3	BiH_3
MP/°C	-77.8	-133.5	-116.3	-88	—
BP/°C	-34.5	-87.5	-62.4	-18.4	$+16.8$ (extrap)
Density/g cm^{-3}(T°C)	0.683 ($-34°$)	0.746 ($-90°$)	1.640 ($-64°$)	2.204 ($-18°$)	—
$\Delta H_f°$/kJ mol^{-1}	-46.1	$-9.6(?)$	66.4	145.1	277.8
Distance (M–H)/pm	101.7	141.9	151.9	170.7	—
Angle H–M–H	107.8°	93.6°	91.8°	91.3°	—

at room temperature, and BiH_3, cannot be kept above $-45°$.

Arsine, AsH_3, is formed when many As-containing compounds are reduced with nascent hydrogen and its decomposition on a heated glass surface to form a metallic mirror formed the basis of Marsh's test for the element. The low-temperature reduction of $AsCl_3$ with $LiAlH_4$ in diethyl ether solution gives good yields of the gas as does the dilute acid hydrolysis of many arsenides of electropositive elements (Na, Mg, Zn, etc.). Similar reactions yield stibine, e.g.:

$$Zn_3Sb_2 + 6H_3O^+ \xrightarrow[\text{14\% yield}]{\text{aq HCl}} 2SbH_3$$
$$+ 3Zn^{2+} + 6H_2O$$

$$SbO_3{}^{3-} + 3Zn + 9H_3O^+ \longrightarrow SbH_3$$
$$+ 3Zn^{2+} + 12H_2O$$

$$SbCl_3(\text{in aq NaCl}) + NaBH_4 \longrightarrow SbH_3$$
$$\text{(high yield)}$$

Both AsH_3 and SbH_3 oxidize readily to the tri-oxide and water, and similar reactions occur with S and Se. AsH_3 and SbH_3 form arsenides and antimonides when heated with metals and this reaction also finds application in semiconductor technology; e.g. highly purified SbH_3 is used as a gaseous *n*-type dopant for Si (p. 332).

Bismuthine, BiH_3, is extremely unstable and was first detected in minute traces by F. Paneth using a radiochemical technique involving $^{212}Bi_2Mg_3$. These experiments, carried out in 1918, were one of the earliest applications of radiochemical tracer experiments in chemistry. Later work using $BH_4{}^-$ to reduce $BiCl_3$ was unsuccessful in producing macroscopic amounts of the gas and the best preparation (1961) is the disproportionation of $MeBiH_2$ at $-45°$ for several hours; Me_2BiH can also be used:

$$Me_{3-n}BiH_n \xrightarrow{-45°} \frac{n}{3}BiH_3 + \frac{3-n}{3}BiMe_3$$
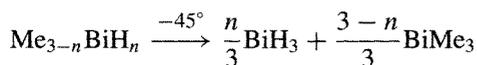
Lower hydrides such as As_2H_4 have occasionally been reported as fugitive species but little is known of their properties (see p. 583;

cf. also N_2H_4, p. 427; P_2H_4, p. 495). Recent fully optimized *ab initio* calculations (including relativistic core potentials) suggest that the double-bonded species $HM{=}MH$ (M = P, As, Sb, Bi) should all exist as *trans* planar (C_{2v}) molecules;[19] close agreement with experimental interatomic distances in known organic diphosphenes (p. 544) and diarsenes adds confidence to the computed distances for $-Sb{=}Sb-$ (260.8 pm) and $-Bi{=}Bi-$ (271.9 pm) which are both about 9% shorter than the corresponding single-bond distances (cf. also $-P{=}P-$ 200.5 pm and $-As{=}As-$ 222.7 pm). The computed bond angles H–M–M in M_2H_2 (M = P, As, Sb, Bi) are 96.2°, 94.4°, 93.0° and 91.8°, respectively.

13.3.3 Halides and related complexes

The numerous halides of As, Sb and Bi show highly significant gradations in physical properties, structure, bonding and chemical reactivity. Distinctions between ionic, coordinate and covalent (molecular) structures in the halides and their complexes frequently depend on purely arbitrary demarcations and are often more a hindrance than a help in discerning the underlying structural and bonding principles. Alternations in the stability of the +5 oxidation state are also illuminating. It will be convenient to divide the discussion into five subsections dealing in turn with the trihalides MX_3, the pentahalides MX_5, other halides, halide complexes of M^{III} and M^V, and oxohalides.

Trihalides, MX_3

All 12 compounds are well known and are available commercially; their physical properties are summarized in Table 13.6 Comparisons with the corresponding data for NX_3 (p. 438) and PX_3 (p. 496) are also instructive. Trends in mp, bp and density are far from regular and reflect the differing structures and bond types.

19 S. NAGASE, S. SUSUKI and T. KURAKAKE, *J. Chem. Soc., Chem. Commun.*, 1724–6 (1990).

Table 13.6 Some physical properties of the trihalides of arsenic, antimony and bismuth

Compound	Colour and state at 25°C	MP/°C	BP/°C	d/g cm^{-3} (T°C)	ΔH_f°/ kJ mol^{-1}
AsF$_3$	Colourless liquid	−6.0	62.8	2.666 (0°)	−956.5
AsCl$_3$	Colourless liquid	−16.2	130.2	2.205 (0°)	−305.0
AsBr$_3$	Pale-yellow crystals	+31.2	221	3.66 (15°)	−197.0
AsI$_3$	Red crystals	140.4	∼400	4.39 (15°)	−58.2
SbF$_3$	Colourless crystals	290	∼345	4.38 (25°)	−915.5
SbCl$_3$	White, deliquescent crystals	73.4	223	3.14 (20°)	−382.2
SbBr$_3$	White, deliquescent crystals	96.0	288	4.15 (25°)	−259.4
SbI$_3$	Red crystals	170.5	401	4.92 (22°)	−100.4
BiF$_3$	Grey-white powder	649[a]	900	∼5.3	−900
BiCl$_3$	White, deliquescent crystals	233.5	441	4.75	−379
BiBr$_3$	Golden, deliquescent crystals	219	462	5.72	−276
BiI$_3$	Green-black crystals	408.6	∼542 (extrap)	5.64	−150

[a]BiF$_3$ is sometimes said to be "infusible" or to have mp at varying temperatures in the range 725–770°, but such materials are probably contaminated with the oxofluoride BiOF (p. 572).

Thus AsF$_3$, AsCl$_3$, AsBr$_3$, SbCl$_3$ and SbBr$_3$ are clearly volatile molecular species, whereas AsI$_3$, SbF$_3$ and BiX$_3$ have more extended interactions in the solid state. Trends in the heats of formation from the elements are more regular being *ca.* −925 kJ mol^{-1} for MF$_3$, *ca.* −350 kJ mol^{-1} for MCl$_3$, *ca.* −245 kJ mol^{-1} for MBr$_3$ and *ca.* −100 kJ mol for MI$_3$. Within these average values, however, AsF$_3$ is noticeably more exothermic than SbF$_3$ and BiF$_3$, whereas the reverse is true for the chlorides; there is also a regular trend towards increasing stability in the sequence As < Sb < Bi for the bromides and for the iodides of these elements.

The trifluorides are all readily prepared by the action of HF on the oxide M$_2$O$_3$ (direct fluorination of M or M$_2$O$_3$ with F$_2$ gives MF$_5$, p. 561). Because AsF$_3$ hydrolyses readily, the reaction is best done under anhydrous conditions using H$_2$SO$_4$/CaF$_2$ or HSO$_3$F/CaF$_2$, but aqueous HF can be used for the others. The trichlorides, tribromides and triiodides of As and Sb can all be prepared by direct reaction of X$_2$ with M or M$_2$O$_3$, whereas the less readily hydrolysed BiX$_3$ can be obtained by treating Bi$_2$O$_3$ with the aqueous HX. Many variants of these reactions are possible: e.g., AsCl$_3$ can be made by chlorination of As$_2$O$_3$ with Cl$_2$, S$_2$Cl$_2$, conc HCl or H$_2$SO$_4$/MCl.

The trihalides of As are all pyramidal molecular species in the gas phase with angle X–As–X in the range 96–100°. This structure persists in the solid state, and with AsI$_3$ the packing is such that each As is surrounded by an octahedron of six I with 3 short and 3 long As–I distances (256 and 350 pm; ratio 1.37, mean 303 pm). The I atoms form a regular hcp lattice. A similar layer structure is adopted by SbI$_3$ and BiI$_3$ but with the metal atoms progressively nearer to the centre of the I$_6$ octahedra:

3 Sb–I at 287 pm and 3 at 332 pm; ratio 1.16, mean 310 pm
all 6 Bi–I at 310 pm; "ratio" 1.00

This is sometimes described as a trend from covalent, molecular AsI$_3$ through intermediate SbI$_3$ to ionic BiI$_3$, but this exaggerates the difference in bond-type. Arsenic, Sb and Bi have very similar electronegativities (p. 550) and it seems likely that the structural trend reflects more the way in which the octahedral interstices in the hcp iodine lattice are filled by atoms of gradually increasing size. The size of these interstices is about constant (see mean M–X distance) but only Bi is sufficiently large to fill them symmetrically.

Discrete molecules are apparent in the crystal structure of the higher trihalides of Sb, and,
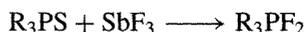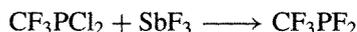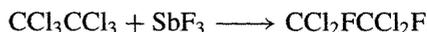
Table 13.7   Structural data for antimony trihalides

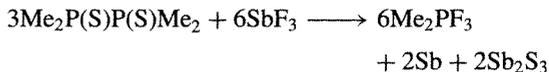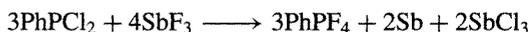|	SbF_3	$SbCl_3$	α-$SbBr_3$	β-$SbBr_3$	SbI_3
Sb–X in gas molecule/pm	?	233	251	251	272
Three short Sb–X in crystal/pm	192	236	250	249	287
Three long Sb–X in crystal/pm	261	$\geq$350	$\geq$375	$\geq$360	332
Ratio (long/short)	1.36	$\geq$1.48	$\geq$1.50	$\geq$1.44	1.16
Angle X–Sb–X in crystal	87°	95°	96°	95°	96°

again, these pack to give 3 longer and 3 shorter interatomic distances (Table 13.7).

The structure of BiF_3 is quite different: β-BiF_3 has the "ionic" YF_3 structure with tricapped trigonal prismatic coordination of Bi by 9 F. $BiCl_3$ has an essentially molecular structure (like SbX_3) but there is a significant distortion within the molecule itself, and the packing gives 5 (not 3) further Cl at 322–345 pm to complete a *bi*capped trigonal prism. As a consequence of this structure $BiCl_3$ has smaller unit cell dimensions than $SbCl_3$ despite the longer Bi–Cl bond (250 pm, as against 236 pm for Sb–Cl). The eightfold coordination has been rationalized by postulating that the ninth position is occupied by the stereochemically active lone-pair of electrons on Bi^{III}. On this basis, the 3 long and 3 short M–X distances in octahedrally coordinated structures can also be understood, the lone-pair being directed towards the centre of the more distant triangle of 3X. However, it is hard to quantify this suggestion, particularly as the X–M–X angles are fairly constant at $97 \pm 2°$ (rather than 109.5° for sp^3 hybrids), implying little variation in hybridization and a lone-pair with substantial s^2 character. The effect is less apparent in SbI_3 and absent BiI_3 (see above) and this parallels the diminishing steric influence of the lone-pair in some of the complexes of the heavier halides with Sn^{II} (p. 380) and Te^{IV} (p. 757).

Many of the trihalides of As, Sb and Bi hydrolyse readily but can be handled without great difficulty under anhydrous conditions. AsF_3 and SbF_3 are important reagents for converting non-metal chlorides to fluorides. SbF_3 in particular is valuable for preparing organofluorine compounds (the Swarts reaction):

$$CCl_3CCl_3 + SbF_3 \longrightarrow CCl_2FCCl_2F$$

$$SiCl_4 + SbF_3 \longrightarrow SiCl_3F, SiCl_2F_2, SiClF_3$$

$$CF_3PCl_2 + SbF_3 \longrightarrow CF_3PF_2$$

$$R_3PS + SbF_3 \longrightarrow R_3PF_2$$

Sometimes the reagents simultaneously act as mild oxidants:

$$3PhPCl_2 + 4SbF_3 \longrightarrow 3PhPF_4 + 2Sb + 2SbCl_3$$

$$3Me_2P(S)P(S)Me_2 + 6SbF_3 \longrightarrow 6Me_2PF_3$$
$$+ 2Sb + 2Sb_2S_3$$

AsF_3, though a weaker fluorinating agent than SbF_3, is preferred for the preparation of high-boiling fluorides since $AsCl_3$ (bp 130°) can be distilled off. SbF_3 is preferred for low-boiling fluorides, which can be readily fractionated from $SbCl_3$ (bp 223°). Selective fluorinations are also possible, e.g.:

$$[PCl_4]^+[PCl_6]^- + 2AsF_3 \longrightarrow [PCl_4]^+[PF_6]^-$$
$$+ 2AsCl_3$$
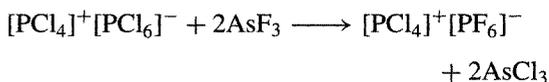
$AsCl_3$ and $SbCl_3$ have been used as non-aqueous solvent systems for a variety of reactions.[20,21] They are readily available, have convenient liquid ranges (p. 559), are fairly easy to handle, have low viscosities η, moderately high dielectric constants ε and good solvent properties (Table 13.8).

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[20] D. S. PAYNE, Chap. 8 in T. C. WADDINGTON (ed.), *Nonaqueous Solvent Systems*, pp. 301–25, Academic Press, London, 1965.

[21] E. C. BAUGHAN, Chap. 5 in J. J. LAGOWSKI (ed.), *The Chemistry of Nonaqueous Solvents*, Vol. 4, pp. 129–65, Academic Press, London, 1976.

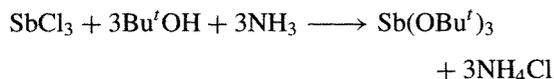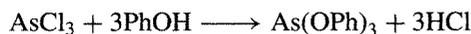**Table 13.8** Some properties of liquid $AsCl_3$ and $SbCl_3$

	η/centipoise	ε	κ/ohm^{-1} cm^{-1}
$AsCl_3$ at 20°C	1.23	12.8	1.4×10^{-7}
$SbCl_3$ at 75°C	2.58	33.2	1.4×10^{-6}

The low conductivities imply almost negligible self-ionization according to the formal scheme:

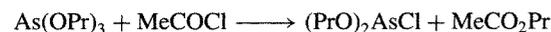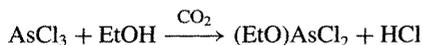$$2MCl_3 \rightleftharpoons MCl_2^+ + MCl_4^-$$

Despite this, they are good solvents for chloride-ion transfer reactions, and solvo-acid–solvo-base reactions (p. 827) can be followed conductimetrically, voltametrically or by use of coloured indicators. As expected from their constitution, the trihalides of As and Sb are only feeble electron-pair donors (p. 198) but they have marked acceptor properties, particularly towards halide ions (p. 564) and amines.

AsX_3 and SbX_3 react with alcohols (especially in the presence of bases) and with sodium alkoxide to give arsenite and antimonite esters, $M(OR)_3$ (cf. phosphorus, (p. 515):

$$AsCl_3 + 3PhOH \longrightarrow As(OPh)_3 + 3HCl$$

$$SbCl_3 + 3Bu^tOH + 3NH_3 \longrightarrow Sb(OBu^t)_3$$
$$+ 3NH_4Cl$$

$$SbCl_3 + 3NaOSiEt_3 \longrightarrow Sb(OSiEt_3)_3 + 3NaCl$$

Halide esters $(RO)_2MX$ and $(RO)MX_2$ can be made similarly:

$$AsCl_3 + 2NaOEt \longrightarrow (EtO)_2AsCl + 2NaCl$$

$$AsCl_3 + EtOH \xrightarrow{CO_2} (EtO)AsCl_2 + HCl$$

$$As(OPr)_3 + MeCOCl \longrightarrow (PrO)_2AsCl + MeCO_2Pr$$

Amino derivatives are obtained by standard reactions with secondary amines, lithium amides or by transaminations:

$$AsCl_3 + 6Me_2NH \longrightarrow As(NMe_2)_3 + 3[Me_2NH_2]Cl$$

$$SbCl_3 + 3LiNMe_2 \longrightarrow Sb(NMe_2)_3 + 3LiCl$$

$$As(NMe_2)_3 + 3Bu_2NH \longrightarrow As(NBu_2)_3 + 3Me_2NH$$

As with phosphorus (p. 533) there is an extensive derivative chemistry of these and related compounds.[15,16]

Pentahalides, MX_5

Until fairly recently only the pentafluorides and $SbCl_5$ were known, but the exceedingly elusive $AsCl_5$ was finally prepared in 1976 by ultraviolet irradiation of $AsCl_3$ in liquid Cl_2 at $-105°C$.[22] Some properties of the 5 pentahalides are given in Table 13.9.

The pentafluorides are prepared by direct reaction of F_2 with the elements (As, Bi) or their oxides (As_2O_3, Sb_2O_3). $AsCl_5$, as noted above, has only a fugitive existence and decomposes to $AsCl_3$ and Cl_2 at about $-50°$. $SbCl_5$ is more stable and is made by reaction of Cl_2 on $SbCl_3$. No pentabromides or pentaiodides have been characterized, presumably because M^V is too highly oxidizing for these heavier halogens (cf. TlI_3, p. 239). The relative instability of $AsCl_5$ when compared with PCl_5 and $SbCl_5$ is a further example of the instability of the highest valency state of p-block elements following the completion of the first (3d) transition series (p. 552). This can be understood in terms of incomplete shielding of the nucleus which leads to a "d-block contraction" and a consequent lowering of the energy of the 4s orbital in As and $AsCl_3$, thereby making it more difficult to promote one of the $4s^2$ electrons

22 K. SEPPELT, *Angew. Chem. Int. Edn. Engl.* **15**, 377–8 (1976).

Table 13.9 Some properties of the known pentahalides

Property	AsF_5	SbF_5	BiF_5	$AsCl_5$	$SbCl_5$
MP/°C	−79.8	8.3	154.4	$\sim$ −50 (d)	4
BP/°C	−52.8	141	230	—	140 (d)
Density $(T°C)$/g cm^{-3}	2.33 (−53°)	3.11 (25°)	5.40 (25°)	—	2.35 (21°)

for the formation of $AsCl_5$. There is no evidence that the As–Cl bond strength itself, in $AsCl_5$, is unduly weak. The non-existence of $BiCl_5$ likewise suggests that it is probably less stable than $SbCl_5$, due the analogous "f-block contraction" following the lanthanide elements (p. 1232).

Evidence from vibration spectroscopy suggests that gaseous AsF_5, solid $AsCl_5$ and liquid $SbCl_5$ are trigonal bipyramidal molecules like PF_5 (D_{3h}), and this is confirmed for AsF_5 by a low-temperature X-ray crystal structure which also indicates that the As-F(axial) distances (171.9 pm) are slightly longer than the As·F (equatorial) distances (166.8 pm).[23] By contrast SbF_5 is an extremely viscous, syrupy liquid with a viscosity approaching 850 centipoise at 20°: the liquid features polymeric chains of *cis*-bridged $\{SbF_6\}$ octahedra in which the 3 different types of F atom (a, b, c) can be distinguished by low-temperature ^{19}F nmr spectroscopy.[24] As shown in Fig. 13.4(a), F_a are the bridging atoms and are *cis* to each other in any one octahedron; F_b are

also *cis* to each other and are, in addition, *cis* to 1 F_a and *trans* to the other, whereas F_c are *trans* to each other and *cis* to both F_a. In the crystalline state the *cis* bridging persists but the structure has tetrameric molecular units (Fig. 13.4(b)) rather than high polymers.[25] There are two different Sb–F–Sb bridging angles, 141° and 170°, and the terminal Sb–F_t distances (mean 182 ± 5 pm) are noticeably less than the bridging Sb–F_μ distances (mean 203 ± 5 pm). (See p. 569 for the ionic structures of Sb_8F_{30}, i.e. $Sb^V_3Sb^{III}_5F_{30}$.) Yet another structure motif is adopted in BiF_5; this crystallizes in long white needles and has the α-UF_5 structure in which infinite linear chains of *trans*-bridged $\{BiF_6\}$ octahedra are stacked parallel to each other. The Bi·F··Bi bridging angle between adjacent octahedra in the chain is 180°.

The pentafluorides are extremely powerful fluorinating and oxidizing agents and they also have a strong tendency to form complexes with electron-pair donors. This latter property has already been presaged by the propensity of SbF_5 to polymerize and is discussed more fully on p. 569.

[23] J. KOHLER, A. SIMON and R. HOPPE, *Z. anorg. allg. Chem.* **575**, 55–60 (1989).

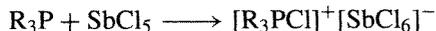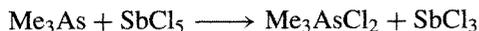[24] T. K. DAVIES and K. C. MOSS, *J. Chem. Soc.*. (A), 1054–8 (1970).

[25] A. J. EDWARDS and P. TAYLOR, *J. Chem. Soc., Chem. Commun.*, 1376–7 (1971).
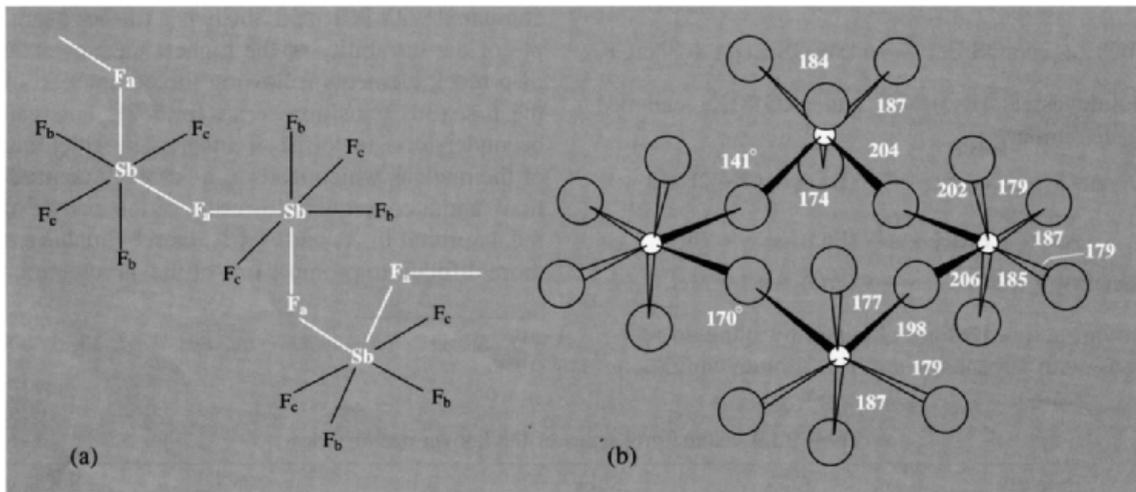
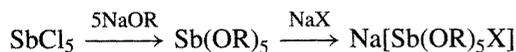**Figure 13.4** (a) The *cis*-bridged polymeric structure of liquid SbF_5 (schematic) showing the three sorts of F atom.[24] (b) Structure of the tetrameric molecular unit in crystalline $(SbF_5)_4$ showing the *cis*-bridging of 4 $\{SbF_6\}$ octahedra (distances in pm).[25]

See also "superacids" on p. 570. Some typical reactions of SbF$_5$ and SbCl$_5$ are as follows:

$$ClCH_2PCl_2 + SbF_5 \longrightarrow ClCH_2PF_4$$

$$Me_3As + SbCl_5 \longrightarrow Me_3AsCl_2 + SbCl_3$$

$$R_3P + SbCl_5 \longrightarrow [R_3PCl]^+[SbCl_6]^-$$

$$(R = Ph, Et_2N, Cl)$$

$$SbCl_5 \xrightarrow{5NaOR} Sb(OR)_5 \xrightarrow{NaX} Na[Sb(OR)_5X]$$

$$(X = OR, Cl)$$

Perhaps the most reactive compound of the group is BiF$_5$. It reacts extremely vigorously with H$_2$O to form O$_3$, OF$_2$ and a voluminous brown precipitate which is probably a hydrated bismuth(V) oxide fluoride. At room temperature BiF$_5$ reacts vigorously with iodine or sulfur; above 50° it converts paraffin oil to fluorocarbons; at 150° it fluorinates UF$_4$ to UF$_6$; and at 180° it converts Br$_2$ to BrF$_3$ and BrF$_5$, and Cl$_2$ to ClF.

Mixed halides and lower halides

Unlike phosphorus, which forms a large number of readily isolable mixed halides of both P^{III} and P^{V}, there is apparently less tendency to form such compounds with As, Sb and Bi, and few mixed halides have so far been characterized. AsF$_3$ and AsCl$_3$ are immiscible below 19°C, but at room temperature ^{19}F nmr indicates some halogen exchange; however equilibrium constants for the formation of AsF$_2$Cl and AsFCl$_2$ are rather small. Likewise, Raman spectra show the presence of AsCl$_2$Br and AsClBr$_2$ in mixtures of the parent trihalides, though rapid equilibration prevents isolation of the mixed halides. It is said that SbBrI$_2$ (mp 88°) can be obtained by eliminating EtBr from EtSbI$_2$Br$_2$.

Mixed pentahalides are more readily isolated and are of at least three types: ionic, tetrameric, and less stable molecular trigonal-bipyramidal monomers. Thus, chlorination of a mixture of AsF$_3$/AsCl$_3$ with Cl$_2$, or fluorination of AsCl$_3$ with ClF$_3$ (p. 828) gives [AsCl$_4$]$^+$[AsF$_6$]$^-$ [mp 130°(d)] whose X-ray crystal structure has recently been redetermined.[26] Similarly, AsCl$_3$ + SbCl$_5$ + Cl$_2$ → [AsCl$_4$]$^+$[SbCl$_6$]$^-$. It also appears that all members of the monomeric molecular series AsCl$_{5-n}$F$_n$ ($n = 1 - 4$) can be made either by thermolysis of [AsCl$_4$]$^+$[AsF$_6$]$^-$ or, in the case of AsCl$_3$F$_2$ (D_{3h}), by gas-solid reaction of AsCl$_2$F$_3$ (g) with CaCl$_2$ (s); the compounds were characterized as trigonal-bipyramidal molecules by low-temperature matrix ir and Raman spectra.[27] The mixed bromofluoride [AsBr$_4$]$^+$[AsF$_6$]$^-$, made by reaction of AsBr$_3$, Br$_2$ and AsF$_5$ at low temperature was also characterized by Raman spectroscopy.[28]

Antimony chloride fluorides have been known since the turn of the century but the complexity of the system, the tendency to form mixtures of compounds, and their great reactivity have conspired against structural characterization until fairly recently.[29] It is now clear that fluorination of SbCl$_5$ depends crucially on the nature of the fluorinating agent. Thus, with AsF$_3$ it gives SbCl$_4$F (mp 83°) which is a cis-F-bridged tetramer as in Fig. 13.4(b) with the terminal F atoms replaced by Cl. Fluorination of SbCl$_5$ with HF also gives this compound but, in addition, SbCl$_3$F$_2$ mp 68° (cis-F-bridged tetramer) and SbCl$_2$F$_3$ mp 62°, which turns out to be [SbCl$_4$]$^+$[Sb$_2$Cl$_2$F$_9$]$^-$. The anion is F-bridged, i.e. [ClF$_4$Sb–F–SbF$_4$Cl]$^-$ with angle Sb–F–Sb 163°. Even more extensive fluorination occurs when SbCl$_5$ is reacted with SbF$_5$ and the product is [SbCl$_4$]$^+$[Sb$_2$F$_{11}$]$^-$. By contrast, fluorination of (SbCl$_4$F)$_4$ with SbF$_5$ in liquid SO$_2$ yields Sb$_4$Cl$_{13}$F$_7$ (mp $\sim$ 50°) which is a cis-F-bridged tetramer of SbCl$_3$F$_2$ with two of the Sb atoms having a Cl atom partially replaced by F, i.e. (Sb$_2$Cl$_{6.5}$F$_{3.5}$)$_2$ and bridge angles Sb–F–Sb of 166–168°.

^{26} R. MINKWITZ, J. NOWICKI and H. BORRMANN, *Z. anorg. allg. Chem.* **596**, 93–8 (1991).

^{27} R. MINKWITZ and H. PRENZEL, *Z. anorg. allg. Chem.* **548**, 103–7 (1987).

^{28} T. KLAPÖTKE, J PASSMORE and E. G. AWERE, *J. Chem. Soc., Chem. Commun.*, 1426–7 (1988).

^{29} J. G. BALLARD, T. BIRCHALL and D. R. SLIM, *J. Chem. Soc., Dalton Trans.*, 62–5 (1979), and references therein.

The attention which has been paid to the mixed chloride fluorides of Sb^V is due not only to the intellectual problem of their structures but also to their importance as industrial fluorinating agents (Swarts reaction). Addition of small amounts of $SbCl_5$ to SbF_5 results in a dramatic decrease in viscosity (due to the breaking of $Sb-F-Sb$ links) and a substantial increase in electrical conductivity (due to the formation of fluoro-complex ions). Such mixed halides are often more effective fluorinating agents than SbF_3, provided that yields are not lowered by oxidation, e.g. $SOCl_2$ gives SOF_2; $POCl_3$ gives $POFCl_2$; and hexachlorobutadiene is partially fluorinated and oxidized to give $CF_3CCl=CClCF_3$ which can then be further oxidized to CF_3CO_2H:

$$CCl_2=CCICCl=CCl_2 \xrightarrow{\text{"}SbF_3Cl_2\text{"}} CF_3CCl=CClCF_3$$

$$\xrightarrow[\text{KOH}]{\text{KMnO}_4/} 2CF_3CO_2H$$
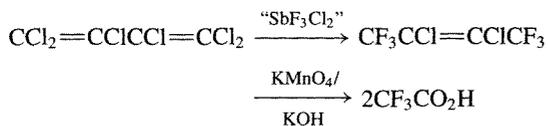
The use of SbF_5 in the preparation of "superacids" such as $(HSO_3F + SbF_5 + SO_3)$ is described in the following subsection (p. 570).

The only well-established lower halide of As is As_2I_4 which is formed as red crystals (mp 137°) when stoichiometric amounts of the 2 elements are heated to 260° in a sealed tube in the presence of octahydrophenanthrene. The compound hydrolyses and oxidizes readily and disproportionates in warm CS_2 solution but is stable up to 150° in an inert atmosphere. Disproportionation is quantitative at 400°:

$$3As_2I_4 \longrightarrow 4AsI_3 + 2As$$
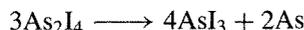
Sb_2I_4 is much less stable: it has been detected by emf or vapour pressure measurements on solutions of Sb in SbI_3 at 230° but has not been isolated as a pure compound.

The lower halides of Bi are rather different. The diatomic species BiX (X = Cl, Br, I) occur in the equilibrium vapour above heated $Bi-BiX_3$ mixtures. A black crystalline lower chloride of composition $BiCl_{1.167}$ is obtained by heating $Bi-BiCl_3$ mixtures to 325° and cooling them during 1–2 weeks to 270° before removing excess $BiCl_3$ by sublimation or extraction into

benzene. The compound is diamagnetic and has an astonishing structure which involves cationic clusters of bismuth and 2 different chloro-complex anions:[30] $[(Bi_9{}^{5+})_2(BiCl_5{}^{2-})_4$-$(Bi_2Cl_8{}^{2-})]$, i.e. $Bi_{24}Cl_{28}$ or Bi_6Cl_7. The $Bi_9{}^{5+}$ cluster is a tricapped trigonal prism (p. 591); the anion $BiCl_5{}^{2-}$ has square pyramidal coordination of the 5 Cl atoms around Bi with the sixth octahedral position presumably occupied by the lone-pair of electrons, and $Bi_2Cl_8{}^{2-}$ has two such pyramids *trans*-fused at a basal edge (p. 565). The compound is stable in vacuum below 200° but disproportionates at higher temperatures. It also disproportionates in the presence of ligands which coordinate strongly to $BiCl_3$ and hydrolyses readily to the oxide chloride.

Bismuth also forms an intriguing family of subiodides, Bi_4I_4, $Bi_{14}I_4$ and $Bi_{18}I_4$, which comprise a series of infinite one-dimensional quasimolecular ribbons of Bi atoms $[Bi_mI_4]_\infty$ of different width ($m = 4, 14, 18$). There are two sorts of Bi atom in these structures: "internal" atoms (Bi_{in}) surrounded by three other Bi atoms only, at 300–312 pm (cf. 307 pm in Bi metal), and "external" Bi_{ex}, connected to differing numbers of Bi and I atoms depending on m.[31] Bi_4Br_4 has a similar structure. The first unambiguous identification of Bi^+ in the solid state came in 1971 when the structure of the complex halide $Bi_{10}Hf_3Cl_{18}$ was shown by X-ray diffraction analysis[32] to be $(Bi^+)(Bi_9{}^{5+})(HfCl_6{}^{2-})_3$. The compound was made by the oxidation of Bi with $HfCl_4/BiCl_3$.

Halide complexes of M^{III} and M^V

The trihalides of As, Sb and Bi are strong halide-ion acceptors and numerous complexes have been isolated with a wide variety of compositions. They are usually prepared by direct reaction of the trihalide with the appropriate

[30] A. HERSHAFT and J. D. CORBETT, *Inorg. Chem.* **2**, 979–85 (1963).

[31] E. V. DIKAREV, B. A. POPOVKIN and A. V. SHEVELKOV, *Z. anorg. allg. Chem.* **612** 118–22 (1992).

[32] R. M. FRIEDMAN and J. D. CORBETT, *J. Chem. Soc., Chem. Commun.*, 422–3 (1971).

(a) (C_{2v}) MX_4^-

(b) $Sb_2F_8^{2-}$ in $NaSbF_4$

(c) $Sb_4F_{16}^{4-}$ in $KSbF_4$
($Sb-F$ 200–230 pm)

(d) 6-coordinate polymeric anion in $pyHSbCl_4$, showing 2 short, 2 intermediate, and 2 long Sb–Cl distances
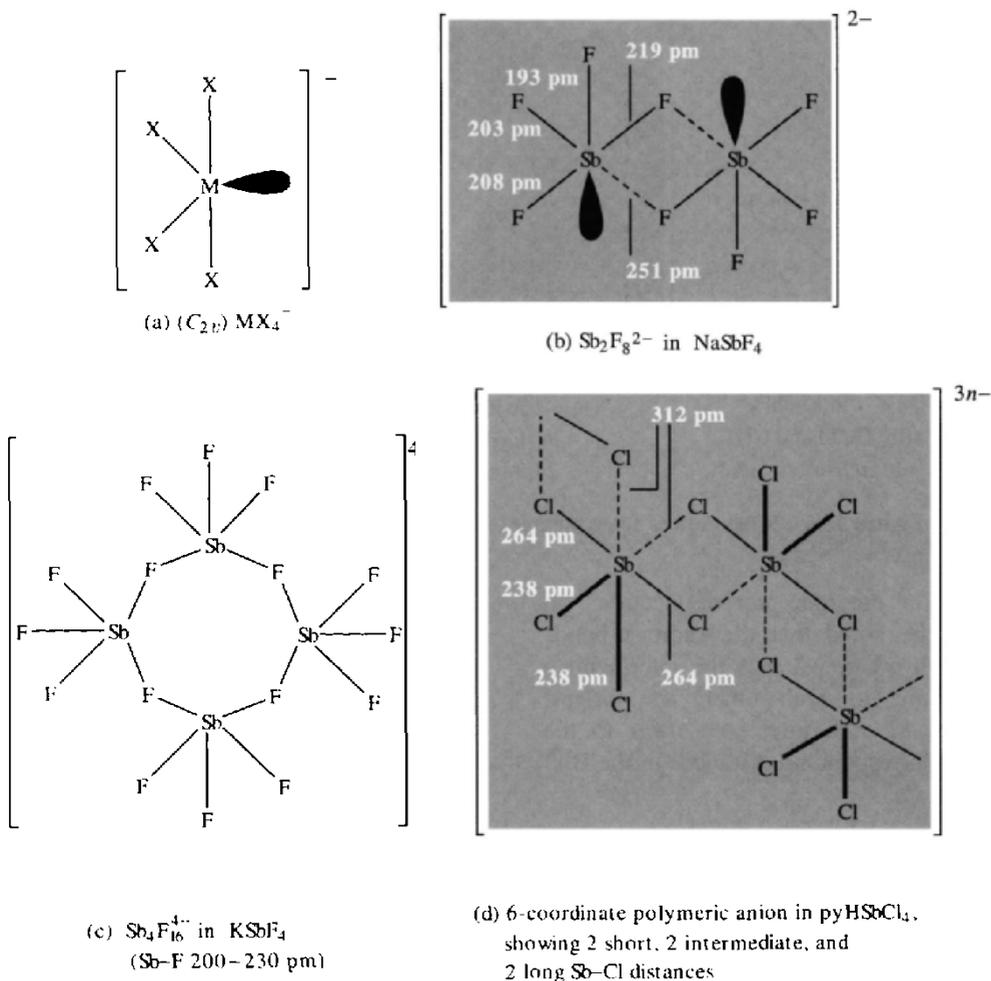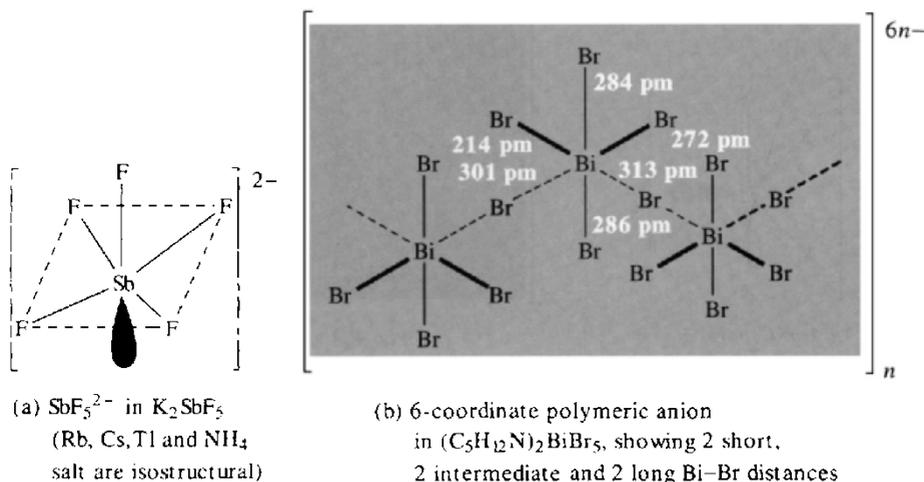
Figure 13.5   Structures of some complex halide anions of stoichiometry MX_4^-

halide-ion donor. However, stoichiometry is not always a reliable guide to structure because of the possibility of oligomerization which depends both on the nature of M and X, and often also on the nature of the counter cation.[16,33] Thus the tetra-alkylammonium salts of MCl_4^-, MBr_4^-, and MI_4^- may contain the monomeric C_{2v} ion as shown in Fig. 13.5a (cf. isoelectronic SeF_4, p. 773), whereas in $NaSbF_4$
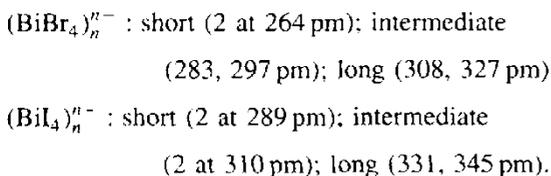
there is a tendency to dimerize by formation of subsidiary $F\cdots Sb$ interactions (Fig. 13.5b) cf. $Bi_2Cl_8^{2-}$ in the preceding subsection. With $KSbF_4$ association proceeds even further to give tetrameric cyclic anions (Fig. 13.5c). In both $NaSbF_4$ and $KSbF_4$ the Sb atoms are 5-coordinate but coordination rises to 6 in the polymeric chain anions of the pyridinium and 2-methylpyridinium salts $pyHSbCl_4$, $(2\text{-}MeC_5H_4NH)BiBr_4$ and $(2\text{-}MeC_5H_4NH)BiI_4$. The structure of $(SbCl_4)_n^{n-}$ is shown schematically in Fig. 13.5d and the three differing Sb–Cl distances reflect, in part,

33 A. F. WELLS, *Structural Inorganic Chemistry*, 5th edn., pp. 879–88 and 894–9, Oxford University Press, Oxford, 1984.

(a) SbF_5^{2-} in K_2SbF_5
(Rb, Cs, Tl and NH_4
salt are isostructural)

(b) 6-coordinate polymeric anion
in $(C_5H_{12}N)_2BiBr_5$, showing 2 short,
2 intermediate and 2 long Bi–Br distances

Figure 13.6 Structures of some complex halide anions of stoichiometry MX_5^{2-}

the influence of the lone-pair of electrons on Sb^{III}. It will be noted that the shortest bonds are *cis* to each other, whereas the intermediate bonds are *trans* to each other; the longest bonds are *cis* to each other and *trans* to the short bonds. Corresponding distances in the Bi^{III} analogues are:

$(BiBr_4)_n^{n-}$: short (2 at 264 pm); intermediate

$\qquad$ (283, 297 pm); long (308, 327 pm)

$(BiI_4)_n^{n-}$: short (2 at 289 pm); intermediate

$\qquad$ (2 at 310 pm); long (331, 345 pm).

Complexes of stoichiometry MX_5^{2-} can feature either discrete 5-coordinate anions as in K_2SbF_5 and $(NH_4)_2SbCl_5$ (Fig. 13.6a), or 6-coordinate polymeric anions as in the piperidinium salt $(C_5H_{10}NH_2)_2BiBr_5$ (Fig. 13.6b). In the discrete anion $SbCl_5^{2-}$ the $Sb-Cl_{apex}$ distance (236 pm) is shorter than the $Sb-Cl_{base}$ distances (2 at 258 and 2 at 269 pm) and the Sb atom is slightly below the basal plane (by 22 pm). The same structure is observed in K_2SbCl_5.

In addition to the various complex fluoroantimonate(III) salts M^ISbF_4 and $M_2^ISbF_5$ mentioned above, the alkali metals form complexes of stoichiometry $M^ISb_2F_7$, $M^ISb_3F_{10}$ and $M^ISb_4F_{13}$, i.e. $[SbF_4 \cdot (SbF_3)_n]$ ($n = 1, 2, 3$)

but the mononuclear complexes $M_3^ISbF_6$ have not been found. The structure of $M^ISb_2F_7$ depends on the strength of the $Sb-F\cdots Sb$ bridge between the 2 units and this, in turn is influenced by the cation. Thus, in KSb_2F_7 there are distorted trigonal-bipyramidal SbF_4^- ions (Fig. 13.7a) and discrete pyramidal SbF_3 molecules (Sb–F 194 pm) with 2 (rather than 3) contacts between these and neighbouring SbF_4^- units of 241 and 257 pm (cf. SbF_3 itself, p. 560). By contrast $CsSb_2F_7$ has well-defined $Sb_2F_7^-$ anions (Fig. 13.7b) formed from 2 distorted trigonal bipyramidal $\{SbF_4\}$ groups sharing a common axial F atom with long bridge bonds.

Similar structural diversity characterizes the heavier halide complexes of the group. The
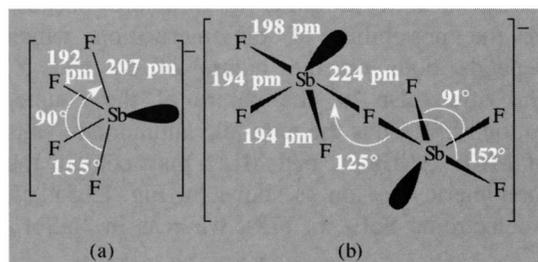
Figure 13.7 Structures of SbF_4^- and $Sb_2F_7^-$ ions in $KSbF_4(SbF_3)$ and $CsSb_2F_7$ respectively.

$[MX_6]^{3-}$ group occurs in several compounds, and these frequently have a regular octahedral structure like the isoelectronic $[Te^{IV}X_6]^{2-}$ ions (p. 776), despite the formal 14-electron configuration on the central atom. For example the jet-black compound $(NH_4)_2SbBr_6$ is actually $[(NH_4^+)_4(Sb^{III}Br_6)^{3-}(Sb^VBr_6)^-]$ with alternating octahedral Sb^{III} and Sb^V ions. The undistorted nature of the $SbBr_6^{3-}$ octahedra suggests that the lone-pair is predominantly $5s^2$ but there is a sense in which this is still stereochemically active since the $Sb-Br$ distance in $[Sb^{III}Br_6]^{3-}$ (279.5 pm) is substantially longer than in $[Sb^VBr_6]^-$ (256.4 pm). Similar dimensional changes are found in $(pyH)_6Sb_4Br_{24}$ which is $[(pyH^+)_6(Sb^{III}Br_6)^{3-}(Sb^VBr_6^-)_3]$. In $(Me_2NH_2)_3BiBr_6$ the $(Bi^{III}Br_6)^{3-}$ octahedron is only slightly distorted. Sixfold coordination also occurs in compounds such as $Cs_3Bi_2I_9$ and $[(pyH^+)_5(Sb_2Br_9)^{3-}(Br^-)_2]$ in which $M_2X_9^{3-}$ has the confacial bioctahedral structure of $Tl_2Cl_9^{3-}$ (p. 240) (Fig. 13.8). In β-$Cs_3Sb_2Cl_9$ and $Cs_3Bi_2Cl_9$, however, there are close-packed Cs^+ and Cl^- with Sb^{III} (or Bi^{III}) in octahedral interstices. In $Cs_3As_2Cl_9$ the $\{AsCl_6\}$ groups are highly distorted so that there are discrete $AsCl_3$ molecules (As–Cl 225 pm) embedded between Cs^+ and Cl^- ions (As–Cl$^-$ 275 pm).

Irregular 6- and 7-fold coordination of Sb occurs in the complexes of $SbCl_3$ with crown thioethers,[34] and 8-fold coordination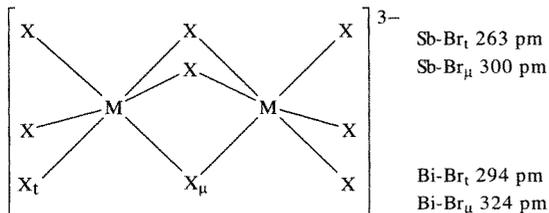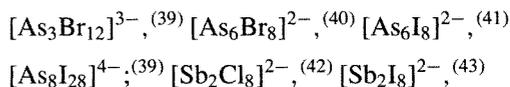 has been established in its complex with the η^5-ether ligand 15-crown-5.[35] Crown ethers have also been used to stabilize the first complexed (9-coordinate) trications of Sb^{III} and Bi^{III}, viz. $[Sb(12\text{-crown-}4)_2(MeCN)]^{3+}[SbCl_6]_3^-$ and $[Bi(12\text{-crown-}4)_2(MeCN)]^{3+}[SbCl_6]_3^-$.[36] The complicated 9- and 10-fold coordination around Bi^{III} in the novel 1:1 and 1:2 arene complexes of $BiCl_3$ with $1,3,5\text{-Me}_3C_6H_3$ (i.e. mesitylene) and C_6Me_6, respectively, should also be noted, viz. $[(\eta^6\text{-mes})_2Bi_2Cl_6]$ in which each Bi is coordinated by $6C + 3Cl + (2Cl)$, and $[(\mu: \eta^6,\eta^6\text{-ar})_2Bi_4Cl_{12}]$ in which each Bi is coordinated by $6C + 2Cl + 2Cl + (2Cl)$ and each C_6Me_6 ligand bridges two Bi atoms.[37] A planar 6-membered $[Bi_3Cl_3]$ ring occurs in $[\{Fe(\eta^5\text{-}C_5H_4Me)(CO)_2\}_2BiCl]_3$.[38]

A fascinating variety of discrete (or occasionally polymeric) polynuclear halogeno complexes of As^{III}, Sb^{III} and Bi have recently been characterized. A detailed discussion would be inappropriate here, but structural motifs include face-shared and edge-shared distorted $\{MX_6\}$ octahedral units fused into cubane-like and other related clusters or cluster fragments. Examples (see also preceding paragraph) are:

$[As_3Br_{12}]^{3-}$,[39] $[As_6Br_8]^{2-}$,[40] $[As_6I_8]^{2-}$,[41]

$[As_8I_{28}]^{4-}$;[39] $[Sb_2Cl_8]^{2-}$,[42] $[Sb_2I_8]^{2-}$,[43]

$$Sb\text{-}Br_t \ 263 \ pm$$
$$Sb\text{-}Br_\mu \ 300 \ pm$$

$$Bi\text{-}Br_t \ 294 \ pm$$
$$Bi\text{-}Br_\mu \ 324 \ pm$$

Figure 13.8 Structure of $M_2X_9^{3-}$

[34] G. R. WILLEY, M. T. LAKIN, M. RAVINDRAN and N. W. ALCOCK, *J. Chem. Soc., Chem. Commun.*, 271–2 (1991).

[35] E. HOUGH, D. G. NICHOLSON and A. K. VASUDEVAN, *J. Chem. Soc., Dalton Trans.*, 427–30 (1987).

[36] R. GARBE, B. VOLLMER, B. NEUMÜLLER, J. PEBLER and K. DENICKE, *Z. anorg. allg. Chem.* **619**, 272–6 (1993).

[37] A. SCHIER, J. M. WALLIS, G. MÜLLER and H. SCHMIDBAUR, *Angew. Chem. Int. Edn. Engl.* **25**, 757–9 (1986).

[38] W. CLEGG, N. A. COMPTON, R. J. ERRINGTON and N. C. NORMAN, *Polyhedron* **6**, 2031–3 (1987). See also W. CLEGG, N. A. COMPTON, R. J. ERRINGTON, G. A. FISHER, C. R. HOCKLESS, N. C. NORMAN and A. G. ORPEN, *Polyhedron* **10**, 123–6 (1991).

[39] W. S. SHELDRICK and H.-J. HÄUSLER, *Angew. Chem. Int. Edn. Engl.* **26**, 1172–4 (1987).

[40] U. MÜLLER and H. SINNINO, *ibid.* **28**, 185–6 (1989).

[41] C. A. GHILARDI, S. MIDOLLINI, S. MONETI and A. ORLANDINI, *J. Chem. Soc., Chem. Commun.*, 1241–2 (1988).

[42] M. G. B. DREW, P. P. K. CLAIRE and G. R. WILLEY, *J. Chem. Soc., Dalton Trans.*, 215–8 (1988).

[43] S. POHL, W. SAAK and D. HASSE, *Angew. Chem. Int. Edn. Engl.* **26**, 467–8 (1987).

Figure 13.9 Schematic representation of the structure of $ISbCl_8$ (see text).

$[Sb_3I_{10}]^-$,[44] $[Sb_3I_{11}]^{2-}$,[45] $[Sb_5I_{18}]^{3-}$,[45,46]

$[Sb_6I_{22}]^{4-}$,[45] $[Sb_8I_{28}]^{4-}$;[46] $[Bi_2I_8L_2]^{2-}$,[47]

$[Bi_4I_{14}L_2]^{2-}$,[48] $[Bi_5I_{19}]^{4-}$,[48] and $[Bi_6I_{22}]^{4-}$.[48]
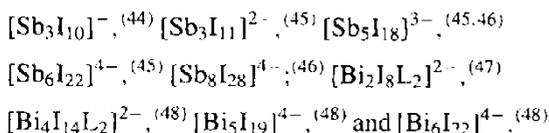
The detailed coordination geometry about As, Sb or Bi in these clusters varies substantially, and is of considerable significance in describing the nature of the bonding in these species.

No completely general and quantitative theory of the stereochemical activity of the lone-pair of electrons in complex halides of tervalent As, Sb and Bi has been developed but certain trends are discernible. The lone-pair becomes less decisive in modifying the stereochemistry (a) with increase in the coordination number of the central atom from 4 through 5 to 6, (b) with increase in the atomic weight of the central atom (As > Sb > Bi), and (c) with increase in the atomic weight of the halogen (F > Cl > Br > I). The relative energies of the various valence-level orbitals may also be an important factor: the $F(\sigma)$ orbital of F lies well below both the s and the p valence orbitals of Sb (for example) whereas the σ orbital energies of Cl, Br and I lie between these two levels, at least in the free atoms. It follows that the lone pair is likely to be in a (stereochemically active) metal-based sp^x hybrid orbital in fluoro complexes of Sb but in a (stereochemically inactive) metal-based a_1 orbital for the heavier halogens.[49]

In the +5 oxidation state, halide complexes of As, Sb and Bi are also well established and the powerful acceptor properties of SbF_5 in particular have already been noted (p. 562). Such complexes are usually made by direct reaction of the pentahalide with the appropriate ligand. Thus $KAsF_6$ and $NOAsF_6$ have octahedral AsF_6^- groups and salts of SbF_6^- and $SbCl_6^-$ (as well as $[Sb(OH)_6]^-$) are also known. Frequently, however, there is strong residual interaction between the "cation" and the "complex anion" and the structure is better thought of as an extended three-dimensional network. For example the adduct $SbCl_5.ICl_3$ (i.e. $ISbCl_8$) comprises distorted octahedra of $\{SbCl_6\}$ and angular $\{ICl_2\}$ groups but, as shown in Fig. 13.9, there is additional interaction between the groups which links them into chains and the structure is intermediate between $[ICl_2]^+[SbCl_6]^-$ and $[SbCl_4]^+[ICl_4]^-$. Complexes are also formed by a variety of oxygen-donors, e.g. $[SbCl_5(OPCl_3)]$ and $[SbF_5(OSO)]$ as

[44] S. POHL, W. SAAK, P. MAYER and A. SCHMIDPETER, *Angew. Chem. Int. Edn. Engl.*, **25**, 825 (1986).
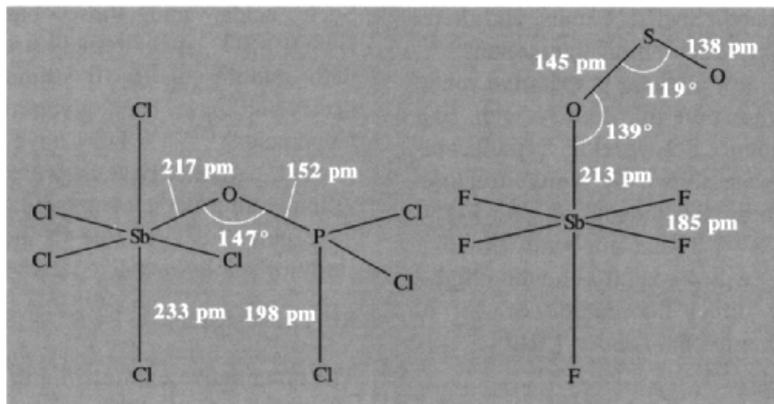
[45] S. POHL, R. LOTZ, W. SAAK and D. HAASE, *ibid.* **28**, 344-5 (1989).

[46] C. J. CAMALT, N. C. NORMAN and L. J. FARRUGIA, *Polyhedron* **12**, 2081-90 (1993).

[47] W. CLEGG, N. C. NORMAN and N. L. PICKETT, *ibid.* **12** 1251-2 (1993).

[48] H. KRAUTSCHIED, *Z. anorg. allg. Chem.* **620**, 1559-64 (1994).

[49] E. SHUSTOROVICH and P. A. DOBOSH, *J. Am. Chem. Soc.* **101**, 4090-5 (1979). B. M. GIMARC, *Molecular Structure and Bonding*, Academic Press, New York, 1979, 240 pp.

Figure 13.10　Schematic representation of the pseudo-octahedral structures of [SbCl$_5$(OPCl$_3$)] and [SbF$_5$(OSO)].

shown in Fig. 13.10. Fluoro-complexes in particular are favoured by large non-polarizing cations, and polynuclear complex anions sometimes then result as a consequence of fluorine bridging. For example irradiation of a mixture of SbF$_5$, F$_2$ and O$_2$ yields white crystals of O$_2$Sb$_2$F$_{11}$ which can be formulated[50] as O$_2$$^+$[Sb$_2F_{11}$]$^-$, and this complex, when heated under reduced pressure at 110°, loses SbF$_5$ to give O$_2$$^+SbF_6$$^-$. The dinuclear anion probably has a linear Sb–F–Sb bridge as in [BrF$_4$]$^+$[Sb$_2$F$_{11}$]$^-$ (p. 834), but in [XeF]$^+$[Sb$_2$F$_{11}$]$^-$ and [XeF$_3$]$^+$[Sb$_2$F$_{11}$]$^-$ (p. 898) the bridging angle is reduced to 150° and 155° respectively. Even more extended coordination occurs in the 1:3 adduct PF$_5$.3SbF$_5$ which has been formulated as [PF$_4$]$^+$[Sb$_3$F$_{16}$]$^-$ on the basis of vibrational spectroscopy.[51] The same anion occurs in the scarlet paramagnetic complex [Br$_2$]$^+$[Sb$_3$F$_{16}$]$^-$ for which X-ray crystallography has established the *trans*-bridged octahedral structure [F$_5$SbFSb(F$_4$)FSbF$_5$]$^-$ with a bridging angle SbF$_\mu$Sb of 148°; the Sb–F$_t$ distances (181–184 pm) are significantly less than the asymmetrical Sb–F$_\mu$ distances (197 and 210 pm 4 pm).[52] The compound (mp 69°) was prepared

by adding a small amount of BrF$_5$ to a mixture of Br$_2$ and SbF$_5$. The structure of the compound AsF$_3$.SbF$_5$ can be described either as a molecular adduct, F$_2$AsF→SbF$_5$, or as an ionic complex, [AsF$_2$]$^+$[SbF$_6$]$^-$; in both descriptions the alternating As and Sb units are joined into an infinite network by further F bonding.[53]

The 1:1 adduct SbF$_3$.SbF$_5$ has the pseudo-ionic structure [Sb$_2^{III}$F$_4$]$^{2+}$[Sb^{V}F$_6$$^-$]$_2$; however, the [F$_2$Sb–F···SbF]$^{2+}$ cation features 5 different Sb–F distances (185, 187, 199, 201 and 215 pm) and can be regarded either as an SbF^{2+} cation coordinated by SbF$_3$, or as a fluorine-bridged dinuclear cation [F$_2$Sb--F–SbF]$^{2+}$, or even as part of an infinite three-dimensional polymer [(SbF$_4$)$_4$]$_n$ when still longer Sb^{III}–F contacts are considered.[54] Several other "adducts" have been prepared leading to the binary fluorides Sb$_3$F$_{11}$, Sb$_4$F$_{14}$, Sb$_7$F$_{29}$, Sb$_8$F$_{30}$ and Sb$_{11}$F$_{43}$. The fluoride Sb$_8$F$_{30}$ (i.e. 5SbF$_3$.3SbF$_5$) is unusual in having more than one structure, depending on its method of preparation. Reduction of SbF$_3$.SbF$_5$ or of SbF$_5$ itself with a stoichiometric amount of PF$_3$ in AsF$_3$ solutions yields crystals of α-Sb$_8$F$_{30}$ comprised of a 3D cross-linked polymeric cation, [Sb$_5$F$_{12}$$^{3+}$]$_\infty$, and [SbF$_6$]$^-$ anions. The polymeric cation can be viewed as strongly interacting

[50] D. E. McKee and N. Bartlett, *Inorg. Chem.* **12**, 2738-40 (1973).

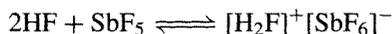[51] G. S. H. Chen and J. Passmore, *J. Chem. Soc., Chem. Commun.*, 559 (1973).

[52] A. J. Edwards and G. R. Jones. *J. Chem. Soc. A* 2318-20 (1971).

[53] A. J. Edwards and R. J. C. Sills, *J. Chem. Soc.* A 942-5 (1971).

[54] R. J. Gillespie, D. R. Slim and J. E. Vekris, *J. Chem. Soc., Dalton Trans.*, 971-4 (1977).
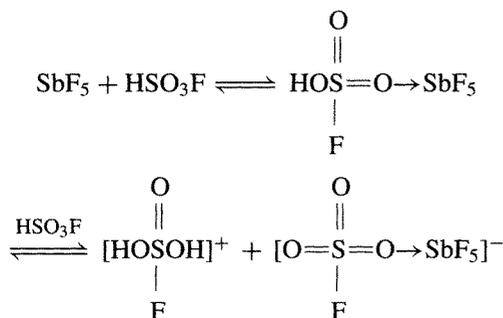
$\{Sb_2F_5\}^+$, $\{SbF_3\}$ and $\{Sb_2F_3\}^{3+}$ units, and there are also significant cation-anion interactions.[55] Alternatively, the less obvious preparative route of oxidative bromination of MeSCN with Br_2 and SbF_5 in liquid SO_2 yields crystals of β-Sb_8F_{30} which were shown by X-ray structure analysis to be best formulated as $[Sb_2F_5]^+$-$[Sb_3F_7]^{2+}[SbF_6]_3^-$.[56] The compound $Sb_{11}F_{43}$ (i.e. $6SbF_3.5SbF_5$) was prepared as a white high-melting solid by direct fluorination of Sb; it contains the polymeric chain cation $[Sb_6F_{13}{}^{5+}]_\infty$ and $[SbF_6]^-$ anions.[57]

The great electron-pair acceptor capacity (Lewis acidity) of SbF_5 has been utilized in the production of extremely strong proton donors (Brønsted acids, p. 48). Thus the acidity of anhydrous HF is substantially increased in the presence of SbF_5:

$$2HF + SbF_5 \rightleftharpoons [H_2F]^+[SbF_6]^-$$

Crystalline compounds isolated from such solutions at $-20°$ to $-30°C$ have been shown by X-ray analysis to be the fluoronium salts $[H_3F_2]^+[Sb_2F_{11}]^-$ and $[H_2F]^+[Sb_2F_{11}]^-$.[58]

An even stronger acid ("Magic Acid") results from the interaction of SbF_5 with an oxygen atom in fluorosulfuric acid HSO_3F (i.e. HF/SO_3):

$$SbF_5 + HSO_3F \rightleftharpoons HOS\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle F}{|}}{=}}O \rightarrow SbF_5$$

$$\overset{HSO_3F}{\rightleftharpoons} [HOSOH]^+ + [O{=}S{=}O \rightarrow SbF_5]^-$$

Such acids, and those based on oleums, $H_2SO_4.nSO_3$, are extremely strong proton donors with acidities up to 10^{12} times that of H_2SO_4 itself, and have been given the generic name 'superacids'.[59-63] They have been extensively studied, particularly as they are able to protonate virtually all organic compounds. In addition, they have played a vital rôle in the preparation and study of stable long-lived carbocations:

$$RH + HSO_3F/SbF_5 \longrightarrow R^+ + [FSO_3.SbF_5]^- + H_2$$

The imaginative exploitation of these and related reactions by G. A. Olah and his group[60-62,64,65] have had an enormous impact on our understanding of organic catalytic processes and on their industrial application, as recognized by the award to Olah of the 1994 Nobel Prize for Chemistry.[66]

Oxide halides

The stable molecular nitrosyl halides NOX (p. 442) and phosphoryl halides POX_3 (p. 501) find few counterparts in the chemistry of As, Sb and Bi. AsOF has been reported as a product of the reaction of As_4O_6 with AsF_3 in a sealed tube at $320°$ but has not been fully characterized. $AsOF_3$ is known only as a polymer. Again, just as $AsCl_5$ eluded preparation for over 140 y after Liebig's first attempt to make it in 1834, so
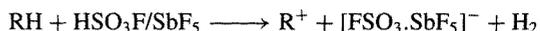
[55] W. A. S. Nandana, J. Passmore, P. S. White and C.-M. Wong, *J. Chem. Soc., Dalton Trans.*, 1989–98 (1987).

[56] R. Minkwitz, J. Nowicki and H. Borrmann, *Z. anorg. allg. Chem.* **605**, 109–16 (1991).

[57] A. J. Edwards and D. R. Slim, *J. Chem. Soc., Chem. Commun.*, 178–9 (1974).

[58] D. Mootz and K. Bartmann, *Angew. Chem. Int. Edn. Engl.* **27**, 391–2 (1988).

[59] R. J. Gillespie, *Acc. Chem. Res.* **1**, 202–9 (1968).

[60] G. A. Olah, A. M. White and D. H. O'Brien, *Chem. Rev.* **70**, 561–91 (1970).

[61] G. A. Olah, G. K. S. Prakash and J. Sommer, *Science* **206**, 13–20 (1979).

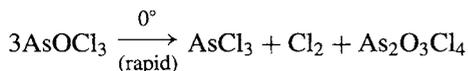[62] G. A. Olah, G. K. S. Prakash, and J. Sommer, *Superacids*, Wiley, New York, 1985, 371 pp.

[63] T. A. O'Donnell, *Superacids and Acidic Melts as Inorganic Chemical Reaction Media*, VCH, New York, 1992, 243 pp.

[64] G. A. Olah, *Aldrichimica Acta* **6**, 7–16 (1973).

[65] G. A. Olah, D. G. Parker and Y. Yoneda, *Angew. Chem. Int. Edn. Engl.* **17**, 909–31 (1978). See also Chapters 1 and 7 in G. A. Olah, G. K. S. Prakash, R. E. Williams L. D. Field and K. Wade, *Hypercarbon Chemistry*, Wiley, New York, 1987, 311 pp.
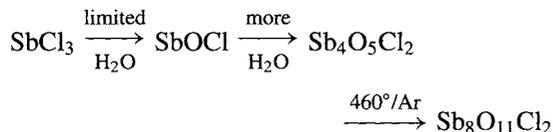
[66] G. A. Olah, *Angew. Chem. Int. Edn. Engl.*, **34**, 1393–405. (Nobel Lecture.)

$AsOCl_3$ defied synthesis until 1976 when it was made by ozonization of $AsCl_3$ in $CFCl_3/CH_2Cl_2$ at $-78°$: it is a white, monomeric, crystalline solid and is one of the few compounds that can be said to contain a "real" $As{=}O$ double bond.[67] $AsOCl_3$ is thermally more stable than $AsCl_5$ (p. 561) but decomposes slowly at $-25°$ to give $As_2O_3Cl_4$:

$$3AsOCl_3 \xrightarrow[\text{(rapid)}]{0°} AsCl_3 + Cl_2 + As_2O_3Cl_4$$

The compound $As_2O_3Cl_4$ is polymeric and is thus not isostructural with $Cl_2P(O)OP(O)Cl_2$.

SbOF and SbOCl can be obtained as polymeric solids by controlled hydrolysis of SbX_3. Several other oxide chlorides can be obtained by varying the conditions, e.g.:

$$SbCl_3 \xrightarrow[H_2O]{\text{limited}} SbOCl \xrightarrow[H_2O]{\text{more}} Sb_4O_5Cl_2$$

$$\xrightarrow{460°/Ar} Sb_8O_{11}Cl_2$$

An alternative dry-way preparation which permits the growth of large, colourless, single crystals suitable for ferroelectric studies (pp. 55–8) has been devised:[68]

$$5Sb_2O_3 + 2SbCl_3 \xrightarrow[\text{vac}]{75°} 3Sb_4O_5Cl_2\,(\text{mp } 590°)$$
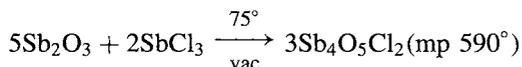
The compounds $Sb_4O_3(OH)_3Cl_2$ and Sb_8OCl_{22} have also been reported. SbOCl itself comprises polymeric sheets of composition $[Sb_6O_6Cl_4]^{2+}$ (formed by linking Sb atoms via O and Cl bridges) interleaved with layers of chloride ions. In addition to polymeric species, finite heterocyclic complexes can also be obtained. For example partial hydrolysis of the polymeric $[pyH]_3[Sb_2^{III}Cl_9]$ in ethanol leads to $[pyH^+]_2[Sb_2^{III}OCl_6]^{2-}$ in which the anion contains 2 pseudo-octahedral $\{{:}SbOCl_4\}$ units sharing a common face $\{\mu_3\text{-}OCl_2\}$ with the lone-pairs *trans* to the bridging oxygen atom
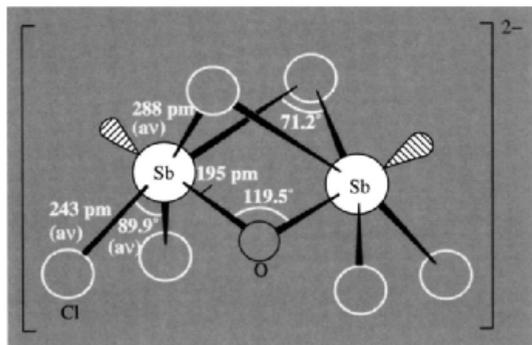
Figure 13.11   Structure of the binuclear anion $[Sb_2^{III}OCl_6]^{2-}$ showing the bridging oxygen and chlorine atoms and the pseudooctahedral coordination about Sb; the O atom is at the common apex of the face-shared square pyramids and the lone-pairs are *trans*- to this below the $\{SbCl_4\}$ bases. The bridging distances $Sb–Cl_\mu$ are substantially longer than the terminal distances $Sb–Cl_t$.

(Fig. 13.11).[69] Another novel polynuclear antimony oxide halide anion has been established in the dark-blue ferrocenium complex $\{[Fe(\eta^5\text{-}C_5H_5)]_2[Sb_4Cl_{12}O]\}_2.2C_6H_6$ which was made by photolysis of benzene solutions of ferrocene (p. 1109) and $SbCl_3$ in the presence of oxygen:[70] the anion (Fig. 13.12) contains 2 square-pyramidal $\{Sb^{III}Cl_5\}$ units sharing a common edge and joined via a unique quadruply bridging Cl atom to 2 pseudo trigonal bipyramidal $\{Sb^{III}Cl_3O\}$ units which share a common bridging O atom and the unique Cl atom. The structure implies the presence of a lone-pair of electrons beneath the basal plane of the first 2 Sb atoms and in the equatorial plane (with O_μ and Cl_t) of the second 2 Sb atoms.

Other finite-complex anions occur in the oxyfluorides. For example the hydrated salts $K_2[As_2F_{10}O].H_2O$ and $Rb_2[As_2F_{10}O].H_2O$

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[67] K. Seppelt, *Angew Chem. Int. Edn. Engl.* **15**, 766–7 (1976).

[68] Ya. P. Kutsenko, *Kristallografiya* (Engl. transl.) **24**, 349–51 (1979).

[69] M. Hall and D. B. Sowerby, *J. Chem. Soc., Chem. Commun.*, 1134–5 (1979).

[70] A. L. Rheingold, A. G. Landers, P. Dahlstrom and J. Zubieta, *J. Chem. Soc., Chem. Commun.*, 143–4 (1979).