

Figure 13.16 Oxidation state diagram for As, Sb and Bi in acid and alkaline solutions, together with selected data on N and P for comparison.

cations and anion vacancies similar to that found in the ordered low-temperature phase of TiO (p. 962).⁽⁸¹⁾ Note that the nominal ionic radii of Li^+ and Bi^{5+} are equal (76 pm). Strong oxidizing agents give brown or black precipitates with alkaline solutions of Bi^{III} , which may be an impure higher oxide, and $NaBi^V O_3$ can be made by heating Na_2O and Bi_2O_3 in O_2 . Such bismuthates of alkali and alkaline earth metals, though often poorly characterized, can be used as strong oxidizing agents in acid solution. Thus Mn in steel can be quantitatively determined by oxidizing it directly to permanganate and estimating the concentration colorimetrically.

13.3.5 Sulfides and related compounds

Despite the venerable history of the yellow mineral orpiment, As_2S_3 , and the orange-red mineral realgar, As_4S_4 (p. 547), it is only during the past two or three decades that the structural interrelation of the numerous arsenic sulfides has emerged. As_2S_3 has a layer-structure analogous to As_2O_3 (p. 574) with each As bonded pyramidally to 3 S atoms at 224 pm and angle S–As–S 99°. It can be made by heating As_2O_3 with S or by passing H_2S into an acidified solution of the oxide. It sublimes readily, even below its mp of 320°, and the vapour has been shown by electron diffraction studies to comprise As_4S_6 molecules isostructural with P_4O_6 (p. 504). The structure can be thought

⁸¹ C. GREAVES and S. M. A. KATIB, *J. Chem. Soc., Chem. Commun.*, 1828–9 (1987).

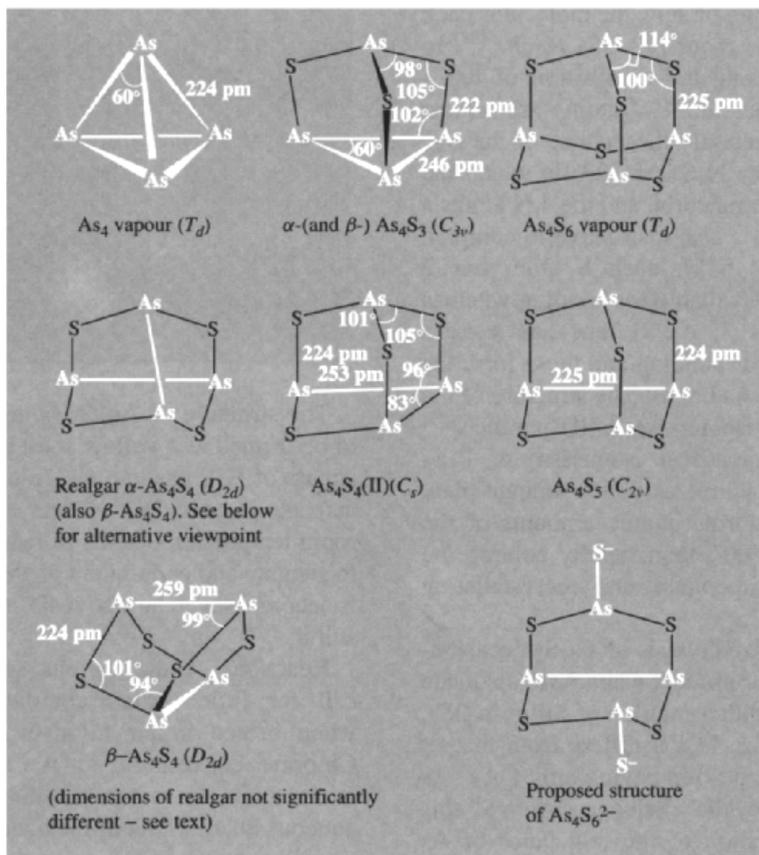


Figure 13.17 Molecular structure of some sulfides of arsenic, stressing the relationship to the As₄ tetrahedron (point group symmetry in parentheses).

of as being derived from the As₄ tetrahedron by placing a bridging S atom above each edge thereby extending the As...As distance to a nonbonding value of ~290 pm. If instead of 6 As–S–As bridges there are 3, 4 or 5, then, as illustrated in Fig. 13.17, the compounds As₄S₃, As₄S₄ (2 isomers) and As₄S₅ are obtained. The molecule As₄S₃ is seen to be isostructural with P₄S₃ and P₄Se₃ (p. 507); it occurs in both the α - and the β -form of the orange-yellow mineral dimorphite (literally “two forms”, discovered by A. Scacchi in volcanic fumaroles in Italy in 1849), the two forms differing only in the arrangement of the molecular units.⁽⁸²⁾ The

compound can be synthesized by heating As and S in the required proportions and purifying the product by sublimation, the β -form being the stable modification at room temperature and the α -form above 130°. The same molecular form occurs in the recently synthesized isoelectronic cationic clusters As₃S₄⁺ (yellow) and As₃Se₄⁺ (orange)⁽⁸³⁾ and in the isoelectronic clusters P₇³⁻, As₇³⁻ and Sb₇³⁻ (p. 588).

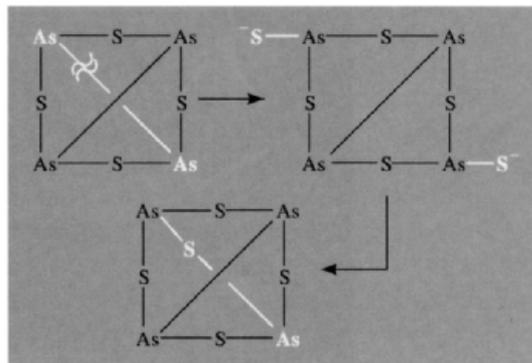
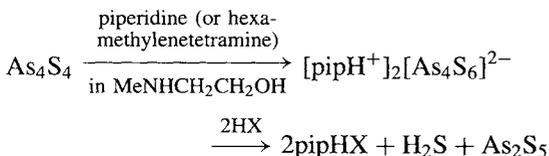
With As₄S₄ there are two possible geometrical isomers of the molecule depending on whether the 2 As–As bonds are skew or adjacent, as shown in Fig. 13.17. Realgar (mp 307°) adopts the more symmetric D_{2d} form with skew As–As

⁸² H. J. WHITFIELD, *J. Chem. Soc. (A)*, 1800–3 (1970); 1737–8 (1973).

⁸³ B. H. CHRISTIAN, R. J. GILLESPIE and J. F. SAWYER, *Inorg. Chem.* **20**, 3410–20 (1981).

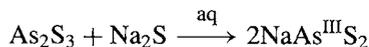
bonds and, depending on how the molecules pack in the crystal, either α - or β -As₄S₄ results.⁽⁸⁴⁾ In addition to the tetrahedral disposition of the 4 As atoms, note that the 4 S atoms are almost coplanar; this is precisely the inverse of the *D*_{2d} structure adopted by N₄S₄ (p. 723) in which the 4 S atoms form a tetrahedron and the 4 N atoms a coplanar square. It is also instructive to compare As₄S₄ with S₈ (p. 655): each S atom has 2 unpaired electrons available for bonding whereas each As atom has 3; As₄S₄ thus has 4 extra valency electrons for bonding and these form the 2 transannular As–As bonds. The structure of the second molecular isomer As₄S₄(II) parallels⁽⁸⁵⁾ the analogous geometrical isomerism of P₄S₄ (p. 507). It was obtained as yellow-orange platy crystals by heating equi-atomic amounts of the elements to 500–600°, then rapidly cooling the melt to room temperature and recrystallizing from CS₂.

Orange needle-like crystals of As₄S₅ occasionally form as a minor product when As₄S₄ is made by heating As₄S₃ with a solution of sulfur in CS₂. Its structure⁽⁸⁶⁾ (Fig. 13.17) differs from that of P₄S₅ and P₄Se₅ (p. 507) in having only 1 As–As bond and no exocyclic chalcogen As=S; this is a further illustration of the reluctance of As to oxidize beyond As^{III} (p. 552). The compound can also be made by heterolytic cleavage of the As₄S₆²⁻ anion. This anion, which is itself made by base cleavage of one of the As–As bonds in realgar, probably has the structure shown in Fig. 13.17 and this would certainly explain the observed sequence of reactions:⁽⁸⁷⁾

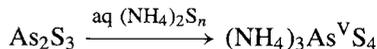


The structure of As₂^VS₅ is unknown. It is said to be formed as a yellow solid by passing a rapid stream of H₂S gas into an ice-cold solution of an arsenate in conc HCl; slower passage of H₂S at room temperature results in reduction of arsenate to arsenite and consequent precipitation of As₂S₃. It decomposes in air above 95° to give As₂S₃ and sulfur.

Reactions of the various sulfides of arsenic call for little further comment. As₂S₃ burns when heated in air to give As₂O₃ and SO₂. Chlorine converts it to AsCl₃ and S₂Cl₂. It is insoluble in water but dissolves readily in aqueous alkali or alkali-metal sulfide solutions to give thioarsenites:



Reacidification reprecipitates As₂S₃ quantitatively. With alkali metal or ammonium polysulfides thioarsenates are formed which are virtually insoluble even in hot conc HCl:



When As₂S₃ is treated with boiling sodium carbonate solution it is converted to As₄S₄; this latter compound can also be made by fusing As₂O₃ with sulfur or (industrially) by heating iron pyrites with arsenical pyrites. As₄S₄ is scarcely attacked by water, inflames in Cl₂, and is used in pyrotechny as it violently enflames when heated with KNO₃. Above about 550° As₄S₄ begins to dissociate reversibly and at 1000° the molecular weight corresponds to As₂S₂ (of unknown structure).

⁸⁴ E. J. PORTER and G. M. SHELDRIK, *J. Chem. Soc., Dalton Trans.*, 1347–9 (1972).

⁸⁵ A. KUTOGLU, *Z. anorg. allg. Chem.* **419**, 176–84 (1976).

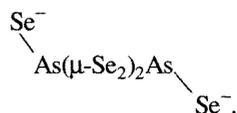
⁸⁶ H. J. WHITFIELD, *J. Chem. Soc., Dalton Trans.*, 1740–2 (1973).

⁸⁷ W. LAUER, M. BECKE-GOEHRING and K. SOMMER *Z. anorg allg. Chem.* **371**, 193–200 (1969).

As_2S_3 and As_4S_4 have also provided a wealth of new ligands for transition-metal complexes, e.g. AsS , AsS_3 , As_2S and, more recently, the geometrically novel bridging η^2, η^2 - SAsSAsS ligand.⁽⁸⁸⁾ Further diversity is emerging with the synthesis and structural characterization of a range of (halogenated)polythiopolyarsenate(III) ions such as cyclo- $[\text{As}_3\text{S}_3\text{X}_4]^-$, (i.e. cyclo- $[(\text{XAs})_3\text{S}_3(\mu_3\text{-X})]^-$; $\text{X} = \text{Cl}, \text{Br}, \text{I}$), cyclo- $[\text{S}=\text{AsS}_5]^-$, bicyclo- $[\text{Br}_2\text{As}(\text{S})_2\text{As}_2(\text{S})_2(\text{CH}_2)]^-$ and $[\text{As}_2\text{SBr}_6]^{2-}$ [i.e. *fac*- $[\text{Br}_2\text{As}(\mu\text{-S}, \text{Br}, \text{Br})\text{AsBr}_2]^{2-}$], all isolated as their $[\text{PPh}_4]^+$ salts.⁽⁸⁹⁾

Three selenides of arsenic are known: As_2Se_3 , As_4Se_3 and As_4Se_4 ; each can be made by direct heating of the elements in appropriate proportions at about 500° followed by annealing at temperatures between $220\text{--}280^\circ$. As_2Se_3 is a stable, brown, semiconducting glass which crystallizes when annealed at 280° ; it melts at 380° and is isomorphous with As_2S_3 . $\alpha\text{-As}_4\text{Se}_3$ forms fine, dark-red crystals isostructural with $\alpha\text{-As}_4\text{S}_3(\text{C}_{3v})$ and the lighter-coloured β -form almost certainly contains the same molecular units.⁽⁹⁰⁾ Similarly, As_4Se_4 is isostructural with realgar, $\alpha\text{-As}_4\text{S}_4$, and the directly linked $\text{As}\text{--}\text{As}$ distances are very similar in the 2 molecules (257 and 259 pm respectively);⁽⁹¹⁾ other dimensions are $\text{As}\text{--}\text{Se}(\text{av})$ 239 pm, angle $\text{Se}\text{--}\text{As}\text{--}\text{Se}$ 95° , angle $\text{As}\text{--}\text{Se}\text{--}\text{As}$ 97° and angle $\text{As}\text{--}\text{As}\text{--}\text{Se}$ 102° (cf. Fig. 13.17). The cationic cluster As_3Se_4^+ was mentioned on p. 579, and the heterocyclic anion $\text{As}_2\text{Se}_6^{2-}$ has been isolated as its orange $[\text{Na}(\text{crypt})]^+$ salt:⁽⁹²⁾ the anion comprises a 6-membered heterocycle $\{\text{As}_2\text{Se}_4\}$ in the chair conformation and each As carries a further exocyclic Se atom to give overall C_{2h}

symmetry, i.e.



Methanolothermal reactions of As_2Se_3 with alkali metal carbonates at 130° yield polymeta-selenoarsenites, MAsSe_2 ($\text{M} = \text{K}, \text{Rb}, \text{Cs}$), in which the polymeric anions consist of tetrahedral $\{\text{AsSe}_3\}$ units linked by corner sharing into infinite chains.⁽⁹³⁾ Complexes of the triangulo- η^3 ligands As_2Se^- and As_2Te^- , such as $[(\text{triphos})\text{Co}(\text{As}_2\text{E})]^+$, can be made by reacting $[\text{Co}(\text{H}_2\text{O})_6]^{2+}[\text{BF}_4]_2^-$ with the appropriate arsenic chalcogenide in the presence of the tridentate ligand $\text{CH}_3\text{C}(\text{CH}_2\text{PPh}_3)_3$, (triphos).⁽⁹⁴⁾

The binary chalcogenides of Sb and Bi are also readily prepared by direct reaction of the elements at $500\text{--}900^\circ$. They have rather complex ribbon or layer-lattice structures and have been much studied because of their semiconductor properties. Both *n*-type and *p*-type materials can be obtained by appropriate doping (pp. 258, 332) and for the compounds M_2X_3 the intrinsic band gap decreases in the sequence $\text{As} > \text{Sb} > \text{Bi}$ for a given chalcogen, and in the sequence $\text{S} > \text{Se} > \text{Te}$ for a given Group 15 element. Some typical properties of these highly coloured compounds are in Table 13.10, but it should be mentioned that mp, density and even colour are often dependent on crystalline form and purity. The large thermoelectric effect of the selenides and tellurides of Sb and Bi finds use in solid-state refrigerators. Sb_2S_3 occurs as the black or steely grey mineral stibnite and is made industrially on a moderately large scale for use in the manufacture of safety matches, military ammunition, explosives and pyrotechnic products, and in the production of ruby-coloured glass. It reacts vigorously when heated with oxidizing agents but is also useful as a pigment in plastics such as

⁸⁸ H. BRUNNER, H. KAUFMANN, B. NUBER, J. WACHTER and M. L. ZIEGLER, *Angew. Chem. Int. Edn. Engl.* **25**, 557–8 (1986) and references cited therein.

⁸⁹ U. MÜLLER and coworkers, *Z. anorg. allg. Chem.* **557**, 91–7 (1987); **566**, 18–24 (1988); **568**, 49–54 (1989); **609**, 82–8 (1992).

⁹⁰ T. J. BASTOW and H. J. WHITFIELD, *J. Chem. Soc., Dalton Trans.*, 959–61 (1977).

⁹¹ T. J. BASTOW and H. J. WHITFIELD, *J. Chem. Soc., Dalton Trans.*, 1739–40 (1973).

⁹² C. H. E. BELIN and M. M. CHARBONNEL, *Inorg. Chem.* **21**, 2504–6 (1982).

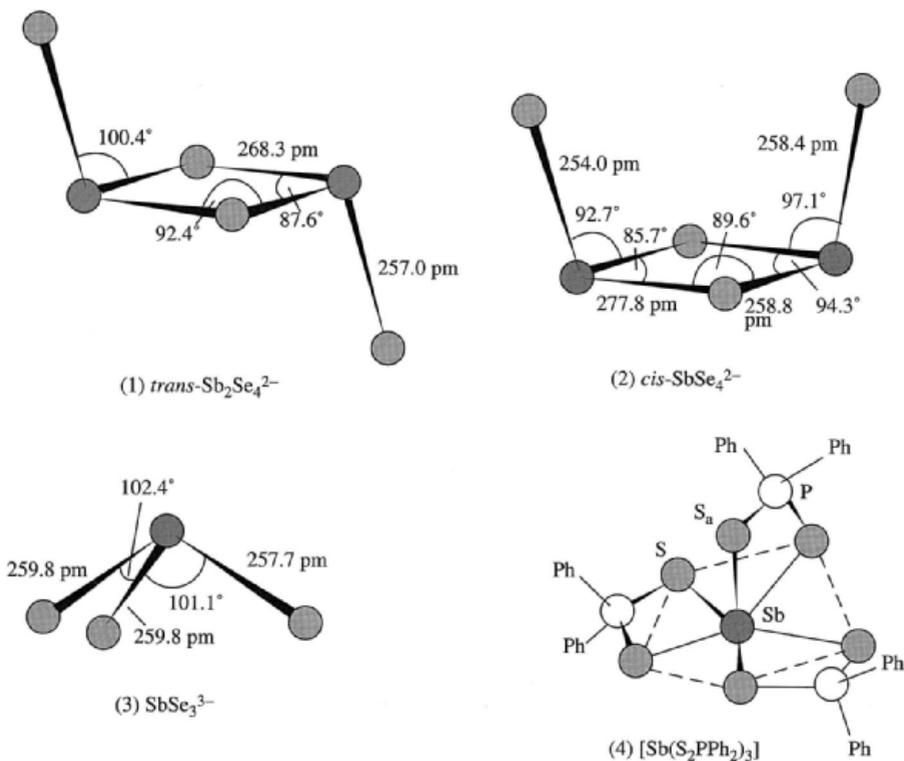
⁹³ W. S. SHELDRIK and H.-J. HÄUSLER, *Z. anorg. allg. Chem.* **561**, 139–48 (1988). See also pp. 149–56 for the similarly prepared $\text{Cs}_3\text{Sb}_5\text{S}_9$ and $\text{Cs}_3\text{Sb}_5\text{Se}_9$.

⁹⁴ M. DI VAIRA, M. PERUZZINI and P. STOPPIONI, *Polyhedron* **5**, 945–50 (1986).

Table 13.10 Some properties of Group 15 chalcogenides M_2X_3

Property	As ₂ S ₃	Sb ₂ S ₃	Bi ₂ S ₃	As ₂ Se ₃	Sb ₂ Se ₃	Bi ₂ Se ₃	As ₂ Te ₃	Sb ₂ Te ₃	Bi ₂ Te ₃
Colour	Yellow	Black	Brown-black	Brown	Grey	Black	Grey	Grey	Grey
MP/°C	320	546	850	380	612	706	360	620	580
Density/g cm ⁻³	3.49	4.61	6.78	4.80	5.81	7.50	6.25	6.50	7.74
E_g /eV ^(a)	2.5	1.7	1.3	2.1	1.3	0.35	~1	0.3	0.15

^(a) 1 eV per atom = 96.485 kJ mol⁻¹.



polythene or polyvinylchloride because of its flame-retarding properties. Golden and crimson antimony sulfides (which comprise mixtures of Sb_2S_3 , Sb_2S_4 and Sb_2OS_3) are likewise used as flame-retarding pigments in plastics and rubbers. A poorly characterized higher sulfide, sometimes said to be Sb_2S_5 , can be obtained as a red solid by methods similar to those outlined for As_2S_5 (p. 580). It is used in fireworks, as a pigment, and to vulcanize red rubber.

Of the more complex chalcogenide derivatives of the Group 15 elements two examples must suffice to indicate the great structural versatility of these elements, particularly

in the +3 oxidation state where the nonbonding electron pair can play an important stereochemical role. Thus, the compound of unusual stoichiometry $\text{Ba}_4\text{Sb}_4^{\text{III}}\text{Se}_{11}$ was found to contain within 1 unit cell: one $trans\text{-}[\text{Sb}_2\text{Se}_4]^{2-}$ (1), two $cis\text{-}[\text{Sb}_2\text{Se}_4]^{2-}$ (2), two pyramidal $[\text{SbSe}_3]^{3-}$ (3), and two Se_2^{2-} ions (Se-Se 236.7 pm) together with the requisite 8 Ba^{2+} cations.⁽⁹⁵⁾ Conversely, the apparently simple 6-coordinate tris(dithiophosphate), $[\text{Sb}(\eta^2\text{-S}_2\text{PPh}_2)_3]$ (4), features pentagonal pyramidal coordination

⁹⁵ G. CORDIER, R. COOK and H. SCHÄFER, *Angew. Chem. Int. Edn. Engl.* **19**, 324–5 (1980).

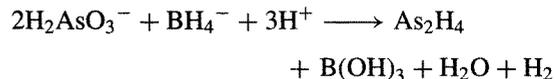
geometry, which is most unusual for a main-group element and may result from the comparatively 'small bite' of the ligand, the lone pair of electrons presumably occupying the seventh coordination position below the pentagonal plane.⁽⁹⁶⁾ The tris(oxalato) anion, $[\text{Sb}^{\text{III}}(\text{C}_2\text{O}_4)_3]^{3-}$, is perhaps the only other example of this geometry.⁽⁹⁷⁾

13.3.6 Metal-metal bonds and clusters

The somewhat limited tendency of N and P to catenate into homonuclear chains has already been noted. The ability to form long chains is even less with As, Sb and Bi, though numerous compounds containing one M-M bond are known and many stable ring and cluster compounds featuring M_n groups have been emerging in recent years. The Group 15 elements therefore differ only qualitatively from C and the other Group 14 elements, on the one hand (p. 374), and S and the Group 16 elements, on the other (p. 751). The elements As, Sb and Bi (like P, p. 487) form well-defined sets of *triangulo*- M_3 and *tetrahedro*- M_4 compounds, whilst Bi in particular has a propensity to form cluster cations Bi_m^{n+} reminiscent of Sn and Pb clusters (p. 394) and *closo*-borane anions (p. 153). Before discussing these various classes of compound, however, it is convenient to recall that a particular grouping of atoms may well have strong interatomic bonds yet still be unstable because of disproportionation into even more stable groupings. A pertinent example concerns the bond dissociation energies of the diatomic molecules of the Group 15 elements themselves in the gas phase. Thus, the ground state electronic configuration of the atoms (ns^2np^3) allows the possibility of triple bonding between pairs of atoms $M_2(\text{g})$, and it is notable that the bond dissociation energy of each of the Group 15 diatomic molecules

is much greater than for those of neighbouring molecules in the same period (Fig. 13.18). Despite this, only N_2 is stable in the condensed phase because of the even greater stability of M_4 or M_{metal} for the heavier congeners (p. 551). A notable advance has, however, been signalled in the isolation and X-ray structural characterization of Sb homologues of N_2 and azobenzene as complex ligands: the red compounds $[(\mu_3\eta^2\text{-Sb}\equiv\text{Sb})\{\text{W}(\text{CO})_5\}_3]$ and $[(\eta^1, \eta^1, (\mu, \eta^2)\text{-PhSb}\equiv\text{SbPh})\{\text{W}(\text{CO})_5\}_3]$ are both stable at room temperature, even on exposure to air.⁽⁹⁸⁾ The dihapto distibene complex $[\text{Fe}(\text{CO})_4(\eta^2\text{-RSb}=\text{SbR})]$ $\{\text{R}=(\text{Me}_3\text{Si})_2\text{CH}\}$ has also been characterized.⁽⁹⁹⁾

Diarsane, As_2H_4 , is obtained in small yield as a byproduct of the formation of AsH_3 when an alkaline solution of arsenite is reduced by BH_4^- upon acidification:



Diarsane is a thermally unstable liquid with an extrapolated bp $\sim 100^\circ$; it readily decomposes at room temperature to a mixture of AsH_3 and a polymeric hydride of approximate composition $(\text{As}_2\text{H})_x$. Sb_2H_4 ($\text{SbCl}_3 + \text{NaBH}_4/\text{dil HCl}$) is even less stable. Both compounds can also be prepared by passing a silent electric discharge through MH_3 gas in an ozonizer at low temperature. Mass spectrometric measurements give the thermochemical bond energy E_{298}° (M-M) as 128 kJ mol^{-1} for Sb_2H_4 and 167 kJ mol^{-1} for As_2H_4 , compared with 183 kJ mol^{-1} for P_2H_4 . Of the halides, As_2I_4 is known (p. 564) but no corresponding compounds of Sb or Bi have yet been isolated (cf. P_2X_4 , p. 497).

Organometallic derivatives M_2R_4 are rather more stable than the hydrides and, indeed, dicacodyl, $\text{Me}_2\text{AsAsMe}_2$, was one of the very first organometallic compounds to be made

⁹⁶ M. J. BEGLEY, D. B. SOWERBY and I. HAIDUC, *J. Chem. Soc., Chem. Commun.*, 64-5 (1980).

⁹⁷ M. D. POORE and D. R. RUSSELL, *J. Chem. Soc., Chem. Commun.*, 18-9 (1971).

⁹⁸ G. HUTTNER, U. WEBER, B. SIGWARTH and O. SCHEIDSTEGE, *Angew. Chem. Int. Edn. Engl.* **21**, 215-6 (1982).

⁹⁹ A. H. COWLEY, N. C. NORMAN, M. PAKULSKI, D. L. BRICKER and D. H. RUSSELL, *J. Am. Chem. Soc.* **107**, 8211-18 (1985).

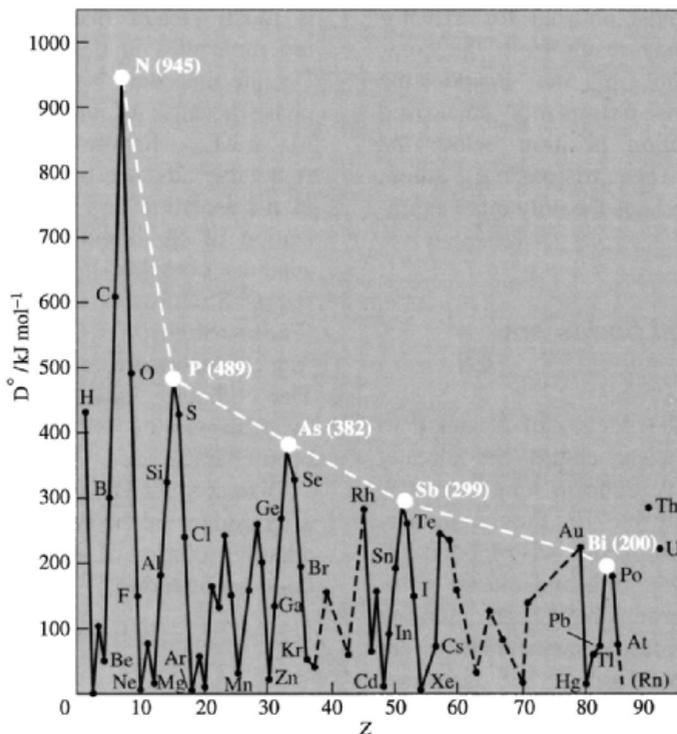
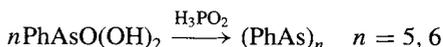
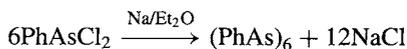


Figure 13.18 Bond dissociation energies for gaseous, homonuclear diatomic molecules (from J. A. Kerr in *Handbook of Chemistry and Physics*, 73rd edn., 1992–3, CRC Press, Boca Raton, Florida), pp. 9.129–9.137.

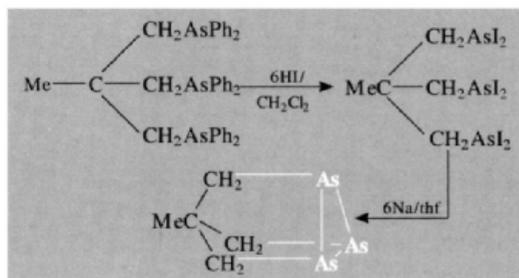
(L. C. Cadet, 1760; R. Bunsen, 1837): it has mp -1° , bp 78° , is extremely poisonous, and has a revolting smell, as indicated by its name (Greek *κακωδία*, *cacodia*, stink). It is now readily made by the reaction of Li metal on Me_2AsI in thf. Other preparative routes to As_2R_4 include reaction of R_2AsH with either R_2AsX or R_2AsNH_2 , and the reaction of R_2AsCl with MASR_2 ($\text{M} = \text{Li}, \text{Na}, \text{K}$). In addition to alkyl derivatives numerous other compounds are known, e.g. As_2Ph_4 mp 127° . $\text{As}_2(\text{CF}_3)_4$ bp 106° has the *trans* (C_{2h}) structure whereas As_2Me_4 has a temperature-dependent mixture of *trans* and *gauche* isomers (p. 428). Corresponding Sb compounds are of more recent lineage, the first to be made (1931) being the yellow crystalline Sb_2Ph_4 mp 122° . Other derivatives have $\text{R} = \text{Me}, \text{Bu}^t, \text{CF}_3, \text{cyclohexyl}, p\text{-tolyl}, \text{cyclopentadienyl}$, etc. Little is known of organodibismuthanes Bi_2R_4 despite sporadic attempts to prepare them.

More extensive catenation occurs in the *cyclo*-polyarsanes $(\text{RAs})_n$ which can readily be prepared from organoarsenic dihalides or from arsonic acids as follows:



In addition to the 6-membered ring in $(\text{PhAs})_6$, 5-membered rings have been obtained with $\text{R} = \text{Me}, \text{Et}, \text{Pr}, \text{Ph}, \text{CF}_3, \text{SiH}_3, \text{GeH}_3$ and 4-membered rings occur with $\text{R} = \text{CF}_3, \text{Ph}$. A 3-membered As_3 ring has also been made and is the first *all-cis* organocyclotriarsane to be characterized.⁽¹⁰⁰⁾

¹⁰⁰ J. ELLERMANN and H. SCHÖSSNER, *Angew. Chem. Int. Edn. Engl.* **13**, 601–2 (1974).



The factors influencing ring size and conformation have not yet become clear. Thus, the yellow $(\text{MeAs})_5$ has a puckered As_5 ring with $\text{As}-\text{As}$ 243 pm and angle $\text{As}-\text{As}-\text{As}$ 102° ; there is also a more stable red form. $(\text{PhAs})_6$ has a puckered As_6 (chair form) with $\text{As}-\text{As}$ 246 pm and angle $\text{As}-\text{As}-\text{As}$ 91° . Numerous polycyclic compounds As_nR_m have also been characterized, for example the bright-yellow crystalline *tricyclo*- $\text{As}_{12}\text{Bu}_8^t$.^(100a)

In view of the excellent donor properties of tertiary arsines, it is of interest to inquire whether these *cyclo*-polyarsanes can also act as ligands. Indeed, $(\text{MeAs})_5$ can displace CO from metal carbonyls to form complexes in which it behaves as a uni-, bi- or tridentate ligand. For example, direct reaction of $(\text{MeAs})_5$ with $\text{M}(\text{CO})_6$ in benzene at 170° ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) yielded red crystalline compounds $[\text{M}(\text{CO})_3(\eta^3\text{-As}_5\text{Me}_5)]$ for which the structure

in Fig. 13.19a has been proposed,⁽¹⁰¹⁾ whereas reaction at room temperature with the ethanol derivative $[\text{M}(\text{CO})_5(\text{EtOH})]$ gave the yellow dinuclear product $[\{\text{M}(\text{CO})_5\}_2\text{-}\mu\text{-}(\eta^1\eta^1\text{-As}_5\text{Me}_5)]$ for which a possible structure is given in Fig. 13.19b. Reaction can also lead to ring degradation; e.g. reaction with $\text{Fe}(\text{CO})_5$ cleaves the ring to give dark-orange crystals of the *catena*-tetraarsane $[\{\text{Fe}(\text{CO})_3\}_2(\text{As}_4\text{Me}_4)]$ whose structure (Fig. 13.20a) has been established by X-ray crystallography.⁽¹⁰²⁾ Even further degradation of the *cyclo*-polyarsane occurs when $(\text{C}_6\text{F}_5\text{As})_4$ reacts with $\text{Fe}(\text{CO})_5$ in benzene at 120° to give yellow plates of $[\text{Fe}(\text{CO})_4\{\text{AsC}_6\text{F}_5\}_2]$ mp 150° (Fig. 13.20b).⁽¹⁰³⁾ In other reactions homoatomic ring expansion or chain extension can occur. For example $(\text{AsMe})_5$ when heated with $\text{Cr}(\text{CO})_6$ in benzene at 150° gives crystals of $[\text{Cr}_2(\text{CO})_6\text{-}\mu\text{-}\{\eta^6\text{-cyclo}(\text{AsMe})_9\}]$, whereas $(\text{AsPr}^n)_5$ and $\text{Mo}(\text{CO})_6$ under similar conditions yield crystals of $[\text{Mo}_2(\text{CO})_6\text{-}\mu\text{-}\{\eta^4\text{-catena}(\text{AsPr}^n)_8\}]$. The molecular structures were determined by X-ray analysis and are shown in Fig. 13.21.⁽¹⁰⁴⁾ In the first, each Cr is 6-coordinate and the As_9 ring is hexahapto, donating 3 pairs of electrons to

^{100a} M. BAUDLER and S. WIETFELDT-HALTENHOFF, *Angew. Chem. Int. Edn. Engl.* **24**, 991-2 (1985).

¹⁰¹ P. S. ELMES and B. O. WEST, *Coord. Chem. Rev.* **3**, 279-91 (1968).

¹⁰² B. M. GATEHOUSE, *J. Chem. Soc., Chem. Commun.*, 948-9 (1969).

¹⁰³ P. S. ELMES, P. LEVERET and B. O. WEST, *J. Chem. Soc., Chem. Commun.*, 747-8 (1971).

¹⁰⁴ P. S. ELMES, B. M. GATEHOUSE, D. J. LLOYD and B. O. WEST, *J. Chem. Soc., Chem. Commun.*, 953-4 (1974).

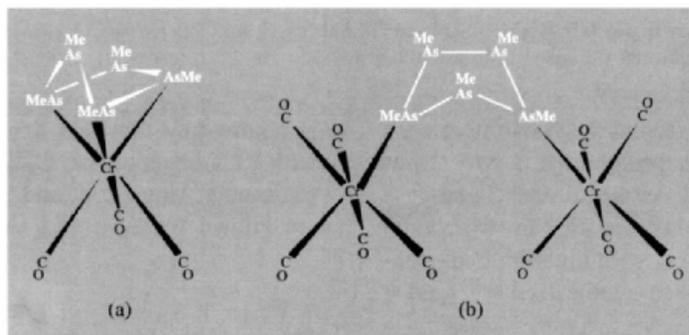


Figure 13.19 Proposed structures for (a) the tridentate *cyclo*-polyarsane complex $[\text{Cr}(\text{CO})_3(\text{As}_5\text{Me}_5)]$, and (b) the bisonodentate binuclear complex $[\{\text{Cr}(\text{CO})_5\}_2(\text{As}_5\text{Me}_5)]$.

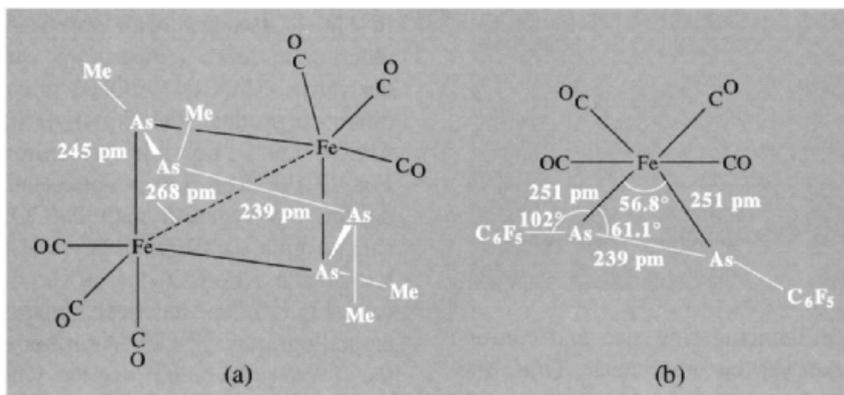


Figure 13.20 Crystal structures of (a) $[\{\text{Fe}(\text{CO})_3\}_2\{(\text{AsMe})_4\}]$, and (b) $[\text{Fe}(\text{CO})_4\{(\text{AsC}_6\text{F}_5)_2\}]$. In (a) the distance between the 2 terminal As atoms is 189 pm, suggesting some “residual interaction” but no direct σ bond.

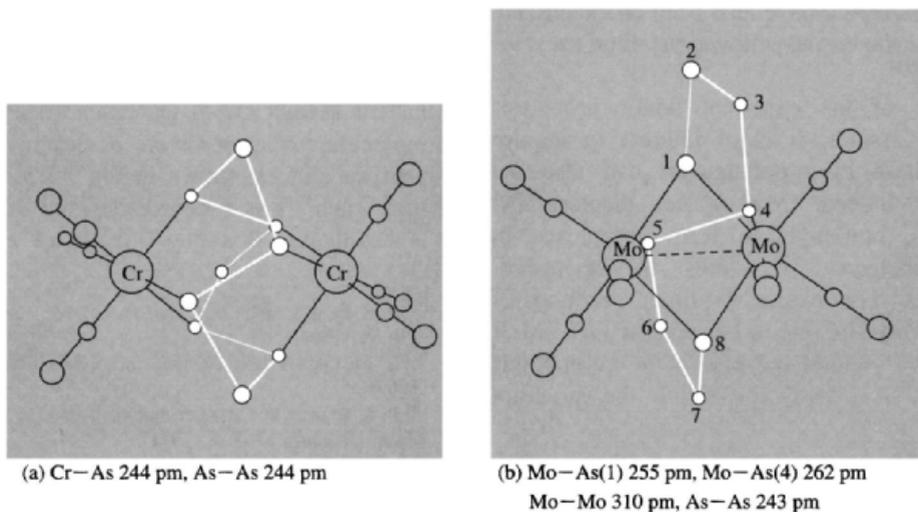


Figure 13.21 Structures of (a) $[\text{Cr}_2(\text{CO})_6-\mu-\{\eta^6\text{-cyclo}(\text{AsMe})_9\}]$, and (b) $[\text{Mo}_2(\text{CO})_6-\mu-\{\eta^4\text{-catena}(\text{AsPr}^n)_8\}]$. In both structures the alkyl group attached to each As atom has been omitted for clarity.

each Cr atom. In the second the As atom at each end of the As_8 chain bridges the 2 Mo atoms whereas the 2 central As atoms each bond to 1 Mo atom only and there is an Mo–Mo bond. Complexes of *cyclo-As*₈ with niobium cyclopentadienyls have also been synthesized,⁽¹⁰⁵⁾ and it

is noteworthy that this ligand is “isoelectronic” with cyclooctatetraene, C_8H_8 . The analogy holds for smaller rings, too, and *cyclo-As*_{*n*} complexes are known for As_3 , As_4 , As_5^- , As_6^- and As_7^- ,

¹⁰⁵ O. J. SCHERER, R. WINTER, G. HECKMANN and G. WOLMERSHÄUSER, *Angew. Chem. Int. Edn. Engl.* **30**, 850–2 (1991). See also H.-G. VON SCHNERING, J. WOLF,

D. WEBER, R. RAMIREZ and T. MEYER, *Angew. Chem. Int. Edn. Engl.* **25**, 353–4 (1986) for the first example of this octahapto *cyclo-As*₈⁸⁻ ligand in the deep red complex $[\text{Rb}(\text{crypt})]^{+}_2[\text{Rb}[\text{Nb}^{\text{V}}\text{As}_8]]^{2-}$ (Nb–As 261–9 pm, As–As 2434 pm, angle AsAsAs 93.7°.

(norbornadiene analogue) as well as for *cyclo*-As₈⁸⁻ (crown-shaped S₈ analogue).

Some of the compounds mentioned in the preceding paragraph can be thought of as heteronuclear cluster compounds and it is convenient to consider here other such heteronuclear cluster species before discussing compounds in which there are homonuclear clusters of Group 15 atoms. Compounds structurally related to the As₄ cluster include the complete series [As_{4-n}{Co(CO)₃}]_n n = 0, 1, 2, 3, 4. It will be noted that the atom As and the group {Co(CO)₃} are “isoelectronic” in the sense that each requires 3 additional electrons to achieve a stable 8- or 18-electron configuration respectively. Yellow crystals of [As₃Co(CO)₃] are obtained by heating (MeAs)₅ with Co₂(CO)₈ in hexane at 200° under a high pressure of CO.⁽¹⁰⁶⁾ The red air-sensitive liquid [As₂{Co(CO)₃}]₂ mp -10° is obtained by the milder reaction of AsCl₃ with Co₂(CO)₈ in thf.⁽¹⁰⁷⁾ Substitution of some carbonyls by tertiary phosphines is also possible under ultraviolet irradiation. Typical structural details are in Fig. 13.22. In the first compound the η³-triangulo-As₃ group can be thought of as a 3-electron donor to the cobalt atom; in the second, the very short As-As bond suggests multiple bonding and the structure closely resembles

that of the “isoelectronic” acetylene complex [{Co(CO)₃}]₂PhC≡CPh] (p. 933). Phosphorus analogues are also known, e.g. the sand-coloured or colourless complexes [M(η³-P₃)L*], where M = Co, Rh or Ir and L* is the tripod-like tris(tertiary phosphine) ligand MeC(CH₂-PPh₂)₃.⁽¹⁰⁸⁾ Likewise the first example of an η²-P₂ ligand symmetrically bonded to 2 metal atoms to give a tetrahedral {P₂Co₂} cluster was established by the X-ray structure determination of [(μ-P₂){Co(CO)₃}{Co(CO)₂(PPh₃)}].⁽¹⁰⁹⁾ If the μ-P₂ (or μ-As₂) ligand is replaced by μ-S₂ (or μ-Se₂), then isoelectronic and isostructural clusters can be obtained by replacing Co by Fe, as in [(μ-S₂){Fe(CO)₃}]₂ and [(μ-Se₂){Fe(CO)₃}]₂ (p. 758).

Even more intriguing are the “double sandwich” complexes which feature {η³-P₃} and {η³-As₃} as symmetrically bridging 3-electron donors. Thus As₄ reacts smoothly with Co^{II} or Ni^{II} aquo ions and the triphosphane ligand L* = MeC(CH₂PPh₂)₃ in thf/ethanol/acetone mixtures to give the exceptionally air-stable dark-green paramagnetic cation [L*Co-μ-(η³-As₃)CoL*]²⁺ with the dimensions shown in Fig. 13.23.⁽¹¹⁰⁾ The structure of the related P₃ complex [L*-μ-(η³-P₃)-NiL*]²⁺ (prepared in the same way using white

¹⁰⁶ A. S. FOUST, M. F. FOSTER and L. F. DAHL, *J. Am. Chem. Soc.* **91**, 5631-3 and 5633-5 (1969).

¹⁰⁷ A. S. FOUST, C. F. CAMPANA, J. D. SINCLAIR and L. F. DAHL, *Inorg. Chem.* **18**, 3047-54 (1979).

¹⁰⁸ C. BIANCHINI, C. MEALLI, A. MELI and L. SACCONI, *Inorg. Chim. Acta* **37**, L543-L544 (1979).

¹⁰⁹ C. F. CAMPANA, A. VIZI-OROSZ, G. PALYI, L. MARKÓ and L. F. DAHL, *Inorg. Chem.* **18**, 3054-9 (1979).

¹¹⁰ M. DI VAIRA, S. MIDOLLINI, L. SACCONI and F. ZANOBINI, *Angew. Chem. Int. Edn. Engl.* **17**, 676-7 (1978).

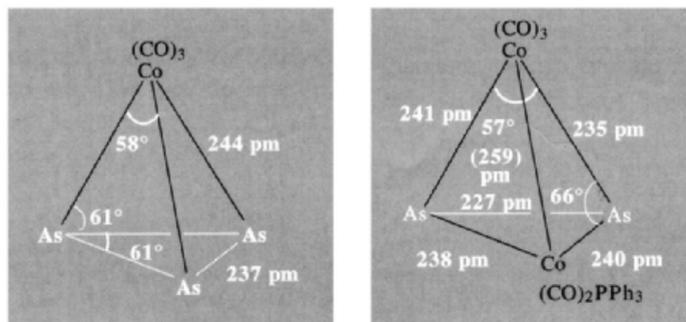


Figure 13.22 Structures of [As₃Co(CO)₃] and [As₂{Co(CO)₃}{Co(CO)₂(PPh₃)}].

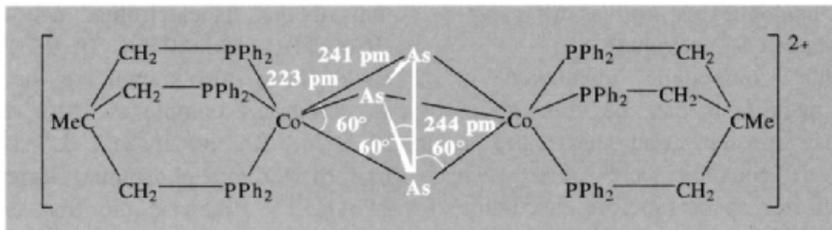


Figure 13.23 Structure of the cation $[L^*Co-\mu-(\eta^3-As_3)CoL^*]^{2+}$.

Table 13.11 Electronic configurations of the isostructural series of complexes containing bridging η^3-P_3 and η^3-As_3 ligands $\{L^*$ is the tridentate tertiary phosphine $MeC(CH_2PPh_2)_3\}$

(η^3-P_3) complex	Colour	Valence electrons	Unpaired electrons	Electrons in highest (e) orbital	Colour	(η^3-As_3) complex
$[L^*_2Co_2(P_3)]^{3+}$	Bright green	30	0	0		$[L^*_2Co_2(As_3)]^{3+}$
$[L^*_2Co_2(P_3)]^{2+}$		31	1	1	Dark green	$[L^*_2Co_2(As_3)]^{2+}$
$[L^*_2Co_2(P_3)]^+$		32	2	2		$[L^*_2Co_2(As_3)]^+$
$[L^*_2CoNi(P_3)]^{2+}$	Red-brown	32	2	2		—
$[L^*_2Ni_2(P_3)]^{2+}$		33	1	3		$[L^*_2Ni_2(As_3)]^{2+}$
$[L^*_2Ni_2(P_3)]^+$	Dark	34	0	4		$[L^*_2Ni_2(As_3)]^+$

P_4) is closely similar⁽¹¹¹⁾ with P–P distances of 216 pm (smaller than for P_4 itself, 221 pm). Indeed, a whole series of complexes has now been established with the same structure-motif and differing only in the number of valency electrons in the cluster; some of these are summarized in Table 13.11.^(111,112) The number of valence electrons in all these complexes falls in the range 30–34 as predicted by R. Hoffmann and his colleagues.⁽¹¹³⁾ Many other cluster types incorporating differing numbers of Group 15 and transition metal atoms are now known and have been fully reviewed.^(114,115)

With Sb even larger clusters can be obtained. For example reaction of $Co(OAc)_2 \cdot 4H_2O$ and

$SbCl_3$ in pentane at 150° under a pressure of H_2/CO gave black crystals of $[Sb_4\{Co(CO)_3\}_4]$ which was found to have a cubane like structure with Sb and Co at alternate vertices of a grossly distorted cube (Fig. 13.24).⁽¹¹⁶⁾

In addition to the heteronuclear clusters considered in the preceding paragraphs, As, Sb and Bi also form homonuclear clusters. We have already seen that alkaline earth phosphides $M_3^{II}P_{14}$ contain the $[P_7]^{3-}$ cluster isoelectronic and isostructural with P_4S_3 , and the analogous clusters $[As_7]^{3-}$ and $[Sb_7]^{3-}$ have also been synthesized. Thus, when As was heated with metallic Ba at $800^\circ C$, black lustrous prisms of Ba_3As_{14} were obtained, isotypic with Ba_3P_{14} ; these contained the $[As_7]^{3-}$ anion with dimensions as shown in Fig. 13.25(a).⁽¹¹⁷⁾ Again,

¹¹¹ M. DI VAIRA, S. MIDOLLINI and L. SACCONI, *J. Am. Chem. Soc.* **101**, 1757–63 (1979).

¹¹² F. FABBRIZZI and L. SACCONI, *Inorg. Chim. Acta*, **36**, L407–L408 (1979).

¹¹³ J. W. LAUHER, M. ELIAN, R. H. SUMMERVILLE and R. HOFFMANN, *J. Am. Chem. Soc.* **98**, 3219–24 (1976).

¹¹⁴ O. J. SCHERER (and 9 others), in R. STEUDEL (ed.), *The Chemistry of Inorganic Ring Systems*, Elsevier, Amsterdam, 1992 pp. 193–208.

¹¹⁵ K. H. WHITMIRE, in H. W. ROESKY (ed.), *Rings, Clusters and Polymers of Main Group and Transition Elements*, Elsevier, Amsterdam, 1989, pp. 503–41.

¹¹⁶ A. S. FOUST and L. F. DAHL, *J. Am. Chem. Soc.* **92**, 7337–41 (1970).

¹¹⁷ W. SCHMETTOW and H. G. VON SCHNERING, *Angew. Chem. Int. Edn. Engl.* **16**, 857 (1977).

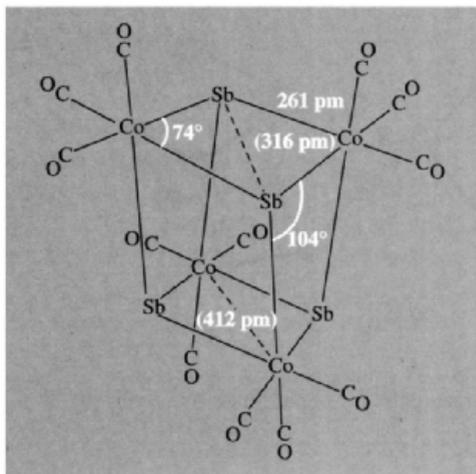


Figure 13.24 Structure of the cubane-like mixed metal-metal cluster $[\text{Sb}_4\text{-Co}(\text{CO})_3]_4$.

when powdered NaSb or NaSb₃ were treated with crypt, $[\text{N}(\text{C}_2\text{H}_4\text{OC}_2\text{H}_4\text{OC}_2\text{H}_4)_3\text{N}]$ (p. 98) in dry ethylenediamine, a deep-brown solution was obtained from which brown needles of $[\text{Na}(\text{crypt})^+]_3[\text{Sb}_7]^{3-}$ were isolated with a C_{3v} anion like $[\text{As}_7]^{3-}$ and Sb-Sb distances 286 pm (base), 270 pm (side) and 278 pm (cap).⁽¹¹⁸⁾

¹¹⁸ J. D. CORBETT, D. G. ADOLPHSON, D. J. MERRIMAN, P. A. EDWARDS and F. J. ARMATIS, *J. Am. Chem. Soc.* **97**, 6267-8 (1975). S. C. CRITCHLOW and J. D. CORBETT, *Inorg.*

Isostructural, neutral molecular clusters can be obtained by replacing the 3 S or 3 Se atoms in P₄S₃ or As₄Se₃ by PR or AsR rather than by P⁻ or As⁻. For example reaction of Na/K alloy with white P₄ and Me₃SiCl in monoglyme gave P₇R₃, P₁₄R₄ and P₁₃R₅. Similarly, Cs₃P₁₁ and Rb₃As₇ react with Me₃SiCl in toluene to give good yields of the bright-yellow crystalline compounds P₁₁(SiMe₃)₃ and As₇(SiMe₃)₃. This latter compound is stable to air and moisture for several hours and has the structure shown in Fig. 13.25b.⁽¹¹⁹⁾ Other examples include As₁₁³⁻⁽¹²⁰⁾ and Sb₁₁³⁻⁽¹²¹⁾ which both have the structure indicated in Fig. 13.26(a). This is very similar to the structure of P₁₁³⁻ [Fig. 12.11(d)] and has approximately D_3 symmetry with eight 3-coordinate As(Sb) atoms forming a bicapped twisted triangular prism with a “waist” of three 2-coordinate bridging atoms. The related As₂₂⁴⁻ anion comprises two such {As₁₁} units conjoined by linking two of these equatorial “waist”

Chem. **23**, 770-4 (1994); this also describes the synthesis and structure of $[\text{K}(\text{crypt})^+]_2[\text{Sb}_4]^{2-}$ which features the square planar $[\text{Sb}_4]^{2-}$ anion with Sb-Sb 275 pm.

¹¹⁹ H. G. VON SCHNERING, D. FENSKE, W. HÖNLE, M. BINNEWIES and K. PETERS, *Angew. Chem. Int. Edn. Engl.* **18**, 679 (1979).

¹²⁰ C. H. E. BELIN, *J. Am. Chem. Soc.* **102**, 6036-40 (1980).

¹²¹ U. BOLLE and W. TREMEL, *J. Chem. Soc., Chem. Commun.*, 91-3 (1992).

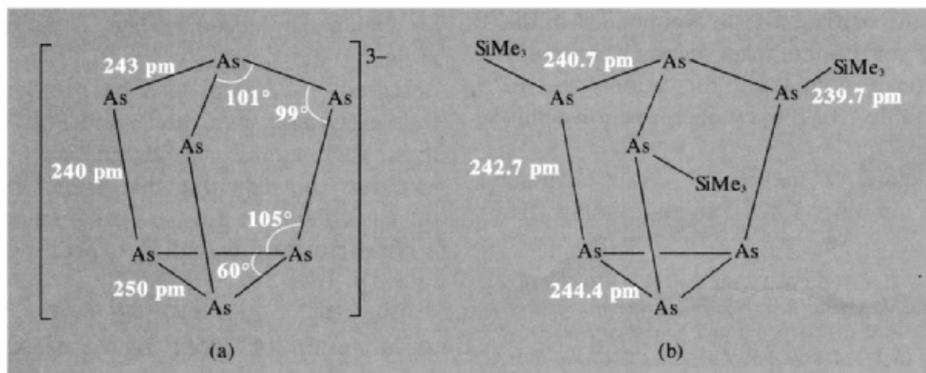


Figure 13.25 (a) Structure of the anion $[\text{As}_7]^{3-}$, isoelectronic with As₄Se₃ (p. 581). The sequence of As-As distances (base>cap>side) is typical for such cluster anions but this alters to the sequence base>side>cap for neutral species such as As₇(SiMe₃)₃ shown in (b).

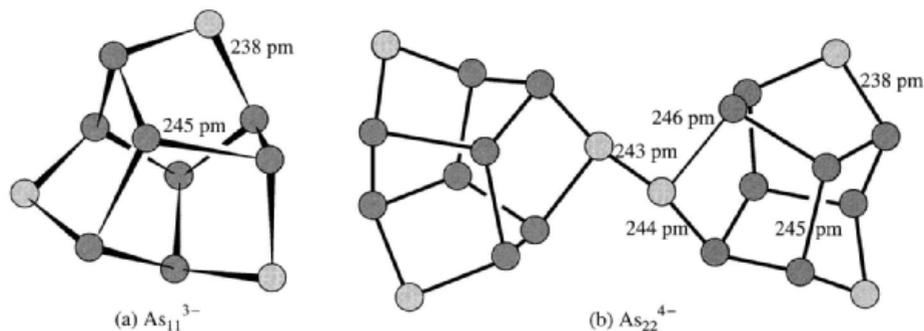


Figure 13.26 (a) Structure of the anion As_{11}^{3-} ; note that the As–As distances involving the three 2-coordinate As atoms are significantly shorter than those between pairs of 3-coordinate As atoms. (b) Structure of the anion As_{22}^{4-} i.e. $[\text{As}_{11}-\text{As}_{11}]^{4-}$ (see text).

atoms as shown in Fig. 13.26(b)⁽¹²²⁾. Many other homonuclear and heteronuclear clusters have also been prepared, of which $[\text{As}_7\text{Se}_4]^{3-}$ ⁽¹²³⁾, $[\text{As}_{10}\text{Te}_3]^{2-}$ ⁽¹²⁴⁾ and $[\text{As}_{11}\text{Te}]^{3-}$ ⁽¹²⁵⁾ can serve as examples. They were made, respectively, by reduction of As_4Se_4 with $\text{K}/\text{C}_2\text{H}_4(\text{NH}_2)_2$ in the presence of $[\text{Ph}_4\text{P}]\text{Br}$, the oxidation of polyarsenides with Te (or reduction of As_2Te_3 with K), and the reaction of the alloy $\text{K}_{1.6}\text{As}_{1.6}\text{Te}$ with a cryptand ligand in ethylenediamine.

In all the cluster compounds discussed above there are sufficient electrons to form 2-centre 2-electron bonds between each pair of adjacent atoms. Such is not the case, however, for the cationic bismuth species now to be discussed and these must be considered as “electron deficient”. The unparalleled ability of Bi/BiCl₃ to form numerous low oxidation-state compounds in the presence of suitable complex anions has already been mentioned (p. 564) and the cationic species shown in Table 13.12 have been unequivocally identified.

The structure of the last 3 cluster cations are shown in Fig. 13.27. In discussing the

structure and bonding of these clusters it will be noted that $\text{Bi}^+(6s^26p^2)$ can contribute 2p electrons to the framework bonding just as {BH} contributes 2 electrons to the cluster bonding in boranes (p. 158). Hence, using the theory developed for the boranes, it can be seen that $[\text{B}_n\text{H}_n]^{2-}$ is electronically equivalent to $(\text{Bi}^+)_n^{2-}$ i.e. $[\text{Bi}_n]^{n-2}$. This would account for the stoichiometries Bi_3^+ and Bi_5^{3+} but would also lead one to expect Bi_8^{6+} and Bi_9^{7+} for the larger clusters. However, these charges are very large and it seems likely that the lowest-lying nonbonding orbital would also be occupied in $(\text{Bi}^+)_n^{2-}$. For $(\text{Bi}^+)_8^{2-}$ this is an e_1 orbital which can accommodate 4 electrons, thereby reducing the charge from Bi_8^{6+} to Bi_8^{2+} as observed. In $(\text{Bi}^+)_9^{2-}$ the lowest nonbonding orbital is a_2'' which can accommodate 2 electrons, thus reducing the charge from Bi_9^{7+} to Bi_9^{5+} as observed.⁽¹²⁶⁾ It will also be noted that Bi_5^{3+} is isoelectronic with Sn_5^{2-} and Pb_5^{2-} (p. 394); these penta-atomic species all have 12 valence electrons (not counting the “inert” s^2 electrons on each atom), i.e. $n+1$ pairs ($n=5$) hence a *closo*-structure would be expected by Wade’s rules (p. 161).

The Bi_9^{5+} ion was discovered in 1963 as a result of work by A. Herschaft and J. D. Corbett on the structure of the black subhalide “BiCl” (p. 564) and subsequently was

¹²² R. C. HAUSHALTER, B. W. EICHHORN, A. L. RHEINGOLD and S. J. GIBB, *J. Chem. Soc., Chem. Commun.*, 1027–8 (1988).

¹²³ V. ANGILELLA H. MERCIA and C. BELIN, *J. Chem. Soc., Chem. Commun.*, 1654–5 (1989).

¹²⁴ R. C. HAUSHALTER, *J. Chem. Soc., Chem. Commun.*, 196–7 (1987).

¹²⁵ C. BELIN and H. MERCIER, *J. Chem. Soc., Chem. Commun.*, 190–1 (1987).

¹²⁶ J. D. CORBETT, *Prog. Inorg. Chem.* **21**, 129–58 (1976).