## 6<sup>th</sup> edition

## Introduction to Modern Inorganic Chemistry

K.M. MacKay, R.A. MacKay, W. Henderson

nelson thornes



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**6th edition** 



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K.M. Mackay R.A. Mackay W. Henderson

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## Preface

Inorganic Chemistry continues to fascinate! The diversity of chemistry covered by the "inorganic" elements brings new and sometimes surprising compounds, insights into the chemistry of biological systems and applications in fields as diverse as polymers and medicine. The overall format of the book closely follows that of previous editions, with the earlier Chapters (1–8 and 13) concentrating on principles, Chapters 9–12, 14 and 15 covering the systematic chemistry of the elements, and the later Chapters (16–20) covering more specialised topics. The Periodic Table continues to be a vital tool in Inorganic Chemistry for the rationalisation and prediction of chemical trends.

In this edition, we have concentrated on a thorough update of material from previous editions, reordering some material, and presenting the material in a modern and readable style by means of boxes, margin notes and many redrawn diagrams. Additional Problems have been added at the end of many chapters as an aid-in-learning for the reader. Topics such as the use of supercritical fluids as solvents, the application of mass spectrometry in inorganic chemistry, carbonyl complexes of metals in high oxidation states, very large metal clusters and the isolation and chemistry of the superheavy elements are an illustration of some of the new and exciting areas which have been added or updated in this edition.

The amount of Inorganic Chemistry knowledge continues to grow at a substantial pace and this is reflected in the large number of journals which report Inorganic Chemistry research. At first, the student may be daunted by the task of finding out information on any particular Inorganic Chemistry topic. To aid this process, we have comprehensively updated the Bibliography, and added a new section on Electronic Sources of Information. The accessibility and power of electronic search tools means that time-consuming literature searches are now a thing of the past; journals themselves are being increasingly accessed in electronic form. Additionally, many excellent books covering general and specialised aspects of Inorganic Chemistry have been published in recent years, and many of these have been included in the reading list.

We are grateful to colleagues, students and readers who have provided us with feedback on previous editions, and are especially grateful to those inorganic chemists whose research is included in this book. We are also very grateful to Professor Martin Ystenes of the Norwegian Institute of Technology, Trondheim.

Ken Mackay Bill Henderson Ann Mackay



### SI UNITS AND NAMES

Units used in this edition The naming of geometrical shapes 3

5

### **SI Units and Names**

Many international scientific and engineering bodies have recommended a unified system of units and the SI (Système International d'Unités) has been generally adopted for use in scientific journals. The full scheme is not universally accepted, and some variant units are found. There are seven basic units:

Physical quantity	Symbol for quantity	Name of unit	Symbol for unit
length	1	metre	m
mass	m	kilogram	kg
time	t	second	S
electric current	Ι	ampere	А
temperature	Т	kelvin	K
amount of substance	n	mole	mol
luminous intensity	$I_{\rm v}$	candela	cđ

Two supplementary units are radian (rad) for plane angles and steradian (sr) for solid angles. The SI system differs from the old metric system by replacing the centimetre and the gram by the metre and the kilogram.

*Multiples* of these units are normally restricted to steps of a thousand, and fractions by steps of a thousandth, i.e. multiples of  $10^{\pm 3}$ , but with the multiples 10,100,1/10 and 1/100 retained.

Fraction	Prefix	Symbol	Multiple	Prefix	Symbol	
10 <sup>-1</sup>	deci	d	10	deca	da	
$10^{-2}$	centi	с	10 <sup>2</sup>	hecto	h	
$10^{-3}$	milli	m	10 <sup>3</sup>	kilo	k	
10 <sup>-6</sup>	micro	μ	10 <sup>6</sup>	mega	М	
10 <sup>-9</sup>	nano	n	10 <sup>9</sup>	giga	G	
$10^{-12}$	pico	р	$10^{12}$	tera	Т	
$10^{-15}$	femto	f	10 <sup>15</sup>	peta	Р	
$10^{-18}$	atto	а	10 <sup>18</sup>	exa	Е	
$10^{-21}$	zepto	z	$10^{21}$	zetta	Ζ	
$10^{-24}$	yocto	у	10 <sup>24</sup>	yotta	Y	

It is important to note that 1 km<sup>2</sup> implies 1 (km)<sup>2</sup>, that is  $10^6$  m<sup>2</sup> and not  $10^3$  m<sup>2</sup>.

A range of units derive from these basic units, or are supplementary to them. Those commonly used by the chemist are shown in Table 1. The unit of force, the newton, is independent of the Earth's gravitation and avoids the introduction of g (the gravitational acceleration) into equations. The unit of energy is the joule (newton  $\times$  metre) and of power, the joule per second (watt).

The gram will be used until a new name is adopted for the kilogram as the basic unit of mass, both as an elementary unit to avoid 'millikilogram', and with prefixes, e.g. mg.

All units not compatible with SI are being abandoned progressively, and the majority of such units are steadily, if slowly, disappearing from the literature. A few units with particular



TABLE 1 Units derived from the basic SI units, or supplementary to them

#### SI UNITS AND NAMES

Name of unit	Symbol and definition
newton pascal joule watt coulomb volt ohm farad hertz degree Celsius (centigrade) square metre cubic metre kilogram per cubic metre metre per second radian per second	Symbol and definition $N = m \text{ kg s}^{-2} \text{ or } J \text{ m}^{-1}$ $Pa = m^{-1} \text{ kg s}^{-2} \text{ or } N \text{ m}^{-2}$ $J = m^2 \text{ kg s}^{-2} \text{ or } N \text{ m}$ $W = m^2 \text{ kg s}^{-3} \text{ or } J \text{ s}^{-1}$ C = sA $V = m^2 \text{ kg s}^{-3} A^{-1} \text{ or } J \text{ s}^{-1} A^{-1}$ $\Omega = m^2 \text{ kg s}^{-3} A^{-2} \text{ or } V A^{-1}$ $F = m^{-2} \text{ kg}^{-1} \text{ s}^4 A^2 \text{ or } s A V^{-1}$ $Hz = s^{-1}$ "C where $t/$ "C = T/K - 273.15 $m^2$ $m^3$ $\text{kg m}^{-3}$ $m \text{ s}^{-1}$ $\text{rad s}^{-1}$
metre per (second) <sup>2</sup> tesla hour, year, etc. will continue to be used	$m s^{-2}$ T = kg s <sup>-2</sup> A <sup>-1</sup> or V s m <sup>-2</sup>
	Name of unit newton pascal joule watt coulomb volt ohm farad hertz degree Celsius (centigrade) square metre cubic metre kilogram per cubic metre metre per second radian per second metre per (second) <sup>2</sup> tesla hour, year, etc. will continue to be used

advantages will probably persist, as any system of units should combine logical consistency with a reasonable degree of convenience. Among such traditional chemical units are:

*Litre*. If multiples are restricted to  $10^{\pm 3}$ , then lengths would be confined to the metre and millimetre, giving volume units of m<sup>3</sup> and mm<sup>3</sup>. It seems unlikely that a system restricted to values differing by  $10^9$  will find favour and the cm<sup>3</sup> and dm<sup>3</sup> are likely to be long with us. It is probable that the litre will survive as a convenient name for the cubic decimetre.

Ångström. The ångström unit  $(10^{-8} \text{ cm} = 10^{-10} \text{ m} = 10^{-1} \text{ nm} = 100 \text{ pm})$  was originally introduced as a unit of length for use on the interatomic scale. It continues to be widely used by crystallographers, though some replacement by the picometre, pm, is occurring.

Atomic mass. This is expressed relative to  ${}^{12}C = 12.0000$  and is termed relative atomic mass, symbol  $A_r$ . Relative molecular mass,  $M_r$ , is the sum of the  $A_r$  values for each atom in the molecule.

Energy. As the joule is of the same order of magnitude, there are no reasons for retaining the calorie. Energies of chemical processes commonly fall into the convenient range of 10 to  $10^3$  kJ mol<sup>-1</sup>, and kcal mol<sup>-1</sup> will disappear. Chemists also use two other units in energy measurement: the *wave number, reciprocal centimetre or Kayser*, written as cm<sup>-1</sup>, and the *electron volt*, eV. The latter is strictly the energy acquired by one electron falling through a potential of one volt, but eV is commonly used for the molar unit found by multiplying the strict value by Avogadro's constant. The main advantages of the electron volt are its close relation to the methods used to measure certain parameters, such as ionization potentials, and its larger size. At about  $10^2$  kJ mol<sup>-1</sup>, it is convenient for the larger chemical energies and its use is likely to continue for many years. The cm<sup>-1</sup> is not a unit of energy but is used in spectroscopy. The relations underlying this application are described in Chapter 7.

The SI system is for reporting precise measurements in a fundamentally self-consistent way, and does not require that other units should never be used. It is not intended to preclude the use of 'working units' and units used in a nonrigorous context. Laboratory workers continue to fractionally distil at pressures measured in millimetres of mercury, autoclave at hundreds of atmospheres and read temperatures in degrees Celsius.

In Table 1 are listed the units which are derived from the basic SI units or their supplements. In Table 2 we list those units which are contrary to SI and are being phased



TABLE 2 Commonly occurring units which are contrary to SI

Un	it	Quantity	Equivalent
(A)	Units differing from SI units by po	wers of 10	
	ångström (Å or A)	length	$10^{-10} \text{ m} = 10^{-1} \text{ nm} = 10^2 \text{ pm}$
	litre (1 or L)	volume	$10^{-3} \text{ m}^3 = \text{dm}^3$
	dyne (dyn)	force	10 <sup>-5</sup> N
	erg	energy	10 <sup>-7</sup> J
	mho (siemens or reciprocal ohm)	conductance	$\Omega^{-1}$
	bar	pressure	10 <sup>5</sup> Pa
	poise	viscosity	0.1 Pa s
	tonne (t)	mass	10 <sup>3</sup> kg
(B)	Other units		
	calorie (cal)	energy	I.T. $cal = 4.1868 J;$
			$15^{\circ}$ cal = 4.1855 J;
			thermochemical cal $= 4.184$ J
	electron volt (eV)	energy	$1.602.1 \times 10^{-19} \text{ J}$
	(electron volt per mole, also symbol	olized $eV = 96.484$	$kJ mol^{-1}$ )
	atmosphere (atm)	pressure	101.325 kN m <sup>-2</sup>
	millimetre of mercury (mmHg) or torr (Torr)	pressure	133.322 N m <sup>-2</sup>
	atomic mass number (amu or $u = 1/12$ mass of ${}^{12}C$ )	mass	$1.66041 \times 10^{-27}$ kg

out. These have conversion factors which are exactly defined, apart from the electron volt and the atomic mass unit which are given in terms of the best experimentally determined factors. The values of physical constants in SI units are listed in Table 3.

### Units used in this edition

A textbook written entirely in SI units faces some disadvantages, particularly as many literature sources still in use are not in SI units and scientists need to be able to convert existing data between systems. With this in mind, the following convention has been adopted in this edition.

Length. The SI system of m, mm, and smaller fractions is used. Notice that many interatomic distances (given originally in ångströms =  $10^{-10}$  m) were known to an accuracy expressed by two decimal places in ångströms, e.g. 1.07 Å. It follows that the most convenient SI-allowed multiple is the picometre, pm, so that values become whole numbers of picometres, e.g. 107 pm, and more accurate values are distinguished by having figures after the decimal point as in 107.6 pm = 1.076 Å. This usage is more convenient than using fractions of the nanometre, as in 0.1076 nm.

Energy. Most values are given in kJ mol<sup>-1</sup> and kcal is not used. Where appropriate,  $cm^{-1}$  and eV are also used and conversion factors are included in tables in these units. Occasionally, particularly when dealing with magnetic resonance, frequencies in Hz are found in place of wave numbers in  $cm^{-1}$ . As 1 Hz is one wave per second and 1  $cm^{-1}$  is one wave per cm, the two are connected by the speed of light. Table 4 shows the interconversion factors for all these units.

*Temperatures*. Temperatures are quoted in degrees Celsius ( $^{\circ}$ C), or in Kelvin (K)—*note* no degree symbol is used.

*Electrical units.* These do not occur widely in this text. Note that the interaction between charges is modified by the permittivity of a vacuum,  $\varepsilon_0$ . Thus the non-SI factors  $e^2/r$ , which occur in the wave equation, for example, now become  $e^2/4\pi\varepsilon_0 r$ .

Other parameters. SI units are used where exact values are stated. Note that the litre is used as the name of the strict SI  $dm^3$ . There is some discussion that the gram-molecule



#### TABLE 3 Values of physical constants

#### SI UNITS AND NAMES

Physical constant	Symbol	Recommended value
Speed of light in a vacuum	<i>C</i> <sub>0</sub>	299 729 458 m s <sup>-1</sup>
Atomic mass unit	ú	$10^{-3}$ kg mol <sup>-1</sup>
		$1.6605655 \times 10^{-27}$ kg
Mass of proton	m <sub>p</sub>	$1.6726231 \times 10^{-27}$ kg
Mass of neutron	m'n	$1.6749543 \times 10^{-27}$ kg
Mass of electron	m <sub>e</sub>	$9.1093897 \times 10^{-31}$ kg
Charge on proton or	e	$1.60217733 \times 10^{-19}$ C
electron (-)		
Boltzmann constant	k or k <sub>B</sub>	$1.380658 imes 10^{-23}$ J K $^{-1}$
Planck constant	h	$6.6260755 imes10^{-34}$ J s
Permeability of a vacuum	$\mu_0$ , 2 = 4 = 3	$4\pi \times 10^{-7} \text{ J s}^2 \text{ C}^{-2} \text{ m}^{-1}$
Rydberg constant	$R_{\infty} = \frac{\mu_0^2 m_e e^2 c^3}{8h^3}$	$1.097373177\times 10^{7}\mathrm{m}^{-1}$
Bohr magneton	$\mu_{\rm B} = \frac{eh}{4\pi m_{\rm e}}$	$9.274078\times10^{-24}~J~T^{-1}$
Avogadro constant	$N_A$ or $L$	$6.0221367  imes 10^{23}mol^{-1}$
Gas constant	R	$8.314510 \text{ J K}^{-1} \text{ mol}^{-1}$
'Ice-point' temperature	$T_{\rm ice}$ or $T_{\rm 0}$	273.150 K
FF	- 108 0	$(RT_0 = 2.271081 \times 10^3 \text{ J mol}^{-1})$
Permittivity of a vacuum	$\varepsilon_0 = (\mu_0 c^2)^{-1}$	$8.85418782 \times 10^{-12}\mathrm{Fm^{-1}}$
Faraday constant	F = Le	$9.648456 \times 10^4 \text{ C mol}^{-1}$
<i>RT</i> in 10/ <i>F</i> at 298 K		$5.916 \times 10^{-2} \text{ V}$
Bohr radius	<b>a</b> 0	$5.2917706 \times 10^{-11}$ m
Molar volume of ideal gas	$V_0 = RT/P_0$	$2.2410383 \times 10^{-2} \text{ m}^3 \text{ mol}^{-1}$
(273.15 K. 1 atm)	· · · · · · · · ·	

#### TABLE 4 Conversion factors

	kJ mol <sup>-1</sup>	cm <sup>-1</sup>	eV	MHz	kcal mol <sup>-1</sup>
kJ mol <sup>-1</sup>	1	83.626	$1.0364 \times 10^{-2}$	$2.5062 \times 10^{6}$	0.2394
$\rm cm^{-1}$	$1.1957 \times 10^{-2}$	1	$1.2394 \times 10^{-4}$	$2.9979 \times 10^4$	$2.858 \times 10^{-3}$
eV	96.484	8068.3	1	$2.4188 \times 10^{8}$	23.063
MHz	$3.9903 \times 10^{-7}$	$3.3356 \times 10^{-5}$	$4.1344 \times 10^{-9}$	1	$9.5345 \times 10^{-8}$
kcal mol <sup>-1</sup>	4.184	349.83	$4.3359 \times 10^{-2}$	$1.0487 \times 10^{7}$	1

might be replaced by the kilogram-molecule but most chemists would find this unacceptable.

In the text, numerical values for physical properties, such as atomic radii or oxidationreduction potentials, are chosen from consistent sets and are quoted mainly for purposes of comparison. Much more accurate values are often available for particular data, and any calculations of physical significance should use such values, which can be found in a number of critical compilations of data or in the original literature.

Formulae are commonly used in place of chemical names where the former are clearer and less clumsy. Equations which are written unbalanced are used either to show the major product of a reaction, or to indicate the variety of products without being definite about their relative proportions. SI UNITS AND NAMES \$eest

S

Η

Κ

d

In addition to the symbols for fundamental constants given in Table 3, a number of other symbols and abbreviations are to be found in the text. These are:

> entropy enthalpy (heat content) equilibrium constant сср cubic close-packed hcp hexagonal close-packed bcc body-centred cube m or m.p. melts or melting point b or b.p. boils or boiling point decomposes subl sublimes

#### 

### The naming of geometrical shapes

Since the geometry of solids was first worked out by the ancient Greeks, much of the terminology comes from Greek and occasionally causes misunderstanding. A regular solid is named for the number of faces, and the Greek root is hedron. Thus the tetrahedron is named for its four faces. The plural is formed by turning *-ron* into *-ra*, and similarly for the adjective. Thus 'tetrahedra' is the plural and 'tetrahedral' the adjective. Since we normally deal with atoms arranged in a geometrical form around a central atom, the chemist is usually more interested in the number of points or *vertices* (note the singular is *vertex*) in a figure, rather than the number of faces. While a tetrahedron has four points and four faces, the number of points and faces differs for all other solids. Thus an octahedron, familiar as the shape found for 6-coordination, has eight faces (hence octa-) and six vertices.

A further relation of interest is that of *capping* which means placing a further atom above a face so that it is at equal distances from each of the atoms which define that face. If we cap planar figures we get pyramids: capping a square gives a square pyramid and capping it again on the other side gives a square *bipyramid*. The capping atom is often termed the apex (plural apices). It may be placed at any distance from the face, but if the distance is equal to the length of the edge of the capped figure, then a special regular shape results. Thus a regularly capped triangle (or regular trigonal pyramid) is a tetrahedron and the octahedron is a regular square bipyramid. If regular figures are capped, further relationships emerge. Thus the eight atoms which regularly cap the faces of an octahedron, themselves form a cube, and if the six faces of a cube are regularly capped, the caps form an octahedron.

We also note some interrelationships involving the cube. If every second vertex of a cube is selected, these four points define a tetrahedron, so a cube may be seen as two identical interpenetrating tetrahedra (see Fig. 13.9). If these two tetrahedra are now altered regularly so that one is elongated and one is compressed (equivalent to pulling two pairs of atoms defining opposite face diagonals out of the face, forming triangles bent about the diagonal) the result is a *dodecahedron*. If a tetrahedron is regularly capped on all four faces, the eight atoms lie at the corners of a cube, the figure resulting corresponds to the formula  $A_4B_4$  and is called a *cubane*.

Finally, one class of less regular figures also occurs among chemical structures—the prisms. A prism is formed by connecting two regular plane figures held in an eclipsed position. For example, a general pentagonal prism has two regular pentagonal faces and five rectangular ones. Again, special figures result if all the edges are equal—a cube is a special case of the square prism, for example. The antiprism is formed if the regular plane figures are placed in a staggered configuration, forming for example a square antiprism. The regular trigonal antiprism is the octahedron.

Examples of all these figures will be found in later chapters. It is extremely valuable to study solid models, or a good computer simulation program, as an aid to understanding the relationships between them.

Table 5 summarizes the properties of the commoner shapes met in chemistry.



TABLE 5 Some common shapes



Ģ













(g)





(1)



A





SI	UNITS	AND	NAMES

Name	Significant geometrical properties	Examples (Figures)
Tetrahedron (a) (for relationship with a	4 faces; 4 points; 6 edges a cube, see Fig. 13.9)	4.3a; 5.1c
Trigonal pyramid	as above, 3 edges longer than others	17.66c
Trigonal bipyramid (b)	6 faces; 5 points; 9 edges	4.4a; 9.8a; 14.29
Square pyramid (c)	4 triangular + 1 square face; 5 points; 8 edges	13.11b; 14.13; 17.66d
Octahedron (d) face-bridged edge-bridged	8 faces; 6 points; 12 edges 8 bridging atoms 12 bridging atoms	4.5a; 5.1a; 15.11 15.19 15.9
Trigonal prism (e)	<ul><li>2 triangular + 3 rectangular faces;</li><li>6 points; 9 edges</li></ul>	5.10c 13.11a
monocapped (f)	cap on rectangular face	15.1
tricapped (g)	caps on all 3 rectangular faces	15.23; 17.40c
Pentagonal pyramid (h)	1 pentagonal + 5 triangular faces; 6 points; 10 edges	9.8b; 14.17a
Pentagonal bipyramid (i)	10 faces; 7 points; 15 edges	14.12; 14.17c
Cube (j) cubane	6 faces; 8 points; 12 edges $A_4B_4$ at alternate vertices	5.1b; 5.12g; 15.16 15.15
Square prism (k)	as cube, four edges different length	14.33
Square antiprism monocapped (l)	2 square + 8 triangular faces; 8 points; 16 edges cap on square face	12.5; 15.5b 18.21



TABLE 5 (Contd.)

(m)

(n)

(0)

(p)

(q)

(r)

#### THE NAMING OF GEOMETRICAL SHAPES

Name	Significant geometrical properties	Examples (Figures
Hexagonal bipyramid (m)	12 faces; 8 points; 18 edges	12.6
Pentagonal antiprism (n)	2 pentagonal + 10 triangular faces; 10 points; 20 edges	16.7a; 16.9
Hexagonal prism (o)	2 hexagonal + 6 rectangular faces; 12 points; 18 edges	5.12e (outline); 16.7b
Octagonal prism (p)	2 octagonal + 8 rectangular edges; 16 points; 24 edges	16.11a
Dodecahedron (q)	12 faces; 8 points; 16 edges	15.2; 15.18
Icosahedron (r)	20 faces; 12 points; 30 edges	17.7d

Note: examples are chosen to give a variety of representations of the shapes.

### References

### 15 CHAPTER 15 THE ELEMENTS OF THE SECOND AND THIRD TRANSITION SERIES

(Compare Co(en) 3 in Section 13.8: also Section

19.2 for metal-sulfur ring compounds). between Pt(NH 3 )6 + and PtXS are known for a variety of amines as well as ammonia, and for X = halogen, OH, NCS, NO 2 , etc. However, fluoride is found only in PtFi~. One very interesting Pt(IV) complex is the sulfide Pt(S 5 )8~ which contains three SS~ units forming PtS 5 six-membered rings by linking into as positions in the octahedron. As this species with three bidentate ligands has nonsuperimposable mirror images, the optical enantiomers may be resolved. The Pt IV octahedral complexes may readily be obtained from the Pt n square-planar complexes if the attacking ligand is also an oxidizing agent. Thus Pt n L 4 +Br 2 →• ¿ra/zs-B^Pt^Li for a variety of ligands (L). The halogen atoms simply add on opposite sides of the square plane. An interesting class of complexes is the deeply coloured, usually green, type of compound which apparently contains trivalent platinum, such as Pt(en)Br 3 or Pt(NH 3 ) 2 Br3. These are not Pt m compounds at all but chains made up of alternate Pt n (NH3) 2 Br2 and Pt IV (NH 3 ) 2 Br4 units as shown in Fig. 15.29. The Pt-Br distances on the vertical axis are 250 pm for Pt IV -Br and 310 pm for the weak Pt 11 - Br interaction. Br Br Br Br-,.. Br . NH 3 •Br ,-NH 3 Br Br Br Br (a) NH 3 Br Br-.. Br\* Br Br+ Br Br Br Br Br Br Br Br (b) FIG. 15.29 Structures of (a) Pt(l\IH 3 ) 2 Br 3 , (b) Pt(en)Br 3 . These structures consist of chains of alternate square-planar platinum(ll) units, PtN 2 Br 2 , and octahedral platinum(IV) units, PtN 2 Br 4 (N = NH 3 or half an ethylenediamine molecule) 15.8.2 The III, II and lower oxidation states As in the example above, many compounds which appear to be in the III state are instead mixed valency ones. Thus PdF 3 is Pd 2+ PdF¿~ and similarly for PtX 3 . The interesting Pt 3 I 8 consists of two octahedral Pt(IV)I 6 units linked to a central square-planar Pt(II)I 4 by shared edges. Hydrated oxides, A/bOs, are reported but their identity is not proven. However, Pd(III) was confirmed in the complex ions Na + [PdF 4 ]  $^{\sim}$  and Ag 3 PdF 6 . In NaK 2 PdF 6 , a structural study shows that the PdFÍ~ ion has four shorter Pd-F bonds of 195 pm, and two longer ones of 214 pm, just as expected for a low-spin d 7 state. Pt(III) has been observed by electron spin resonance after X-irradiation of a -Pt(II) complex, [Pt(en) 2 ] 2+ , in the presence of a large anión. CHAPTER 15 PALLADIUM, 4a <sup>°</sup>5s<sup>°</sup>, AND PLATINUM, 5d 6s 381

\p/j In a second class of formally + III compounds, a Pd-Pd or Pt-Pt bond exists in a dimer in / ∖ compounds of the type X-Pt(bident) n Pt-X. Here bident = a bidentate ligand which bridges C ' NX / the two Pt atoms, holding them close enough together for a Pt-Pt bond to form. The M(III) Pd compounds are made when the bridged Pt(II) complexes are treated with X 2 (compare the Ci ci analogous gold compounds, Fig. 15.32). There may be between n = 2 and n = 4 bidentate ^p// groups present. Such Pt(III) compounds are well established and a few Pd analogues are / \ known. More recently a Pt(III) species with an unsupported Pt-Pt bond has been found in Cl x y 01 the complex ion [(CN) 5 Pt-Pt(CN) 5 ] 4 ". Pd Like nickel, these elements have a very stable II state, but occur only in the squareCi ci planar configuration in this state. All the dihalides except PtF 2 are found. Palladium forms a \p/f stable PdO while platinum gives a hydrated PtO which readily oxidizes to Pt0 2 . Palladium / \ dichloride has a chain structure of linked square-planar PdCl 4 units. CI £l A second form of palladium dichloride, and the only form of the platinum compound, Pd consists of M 6 Cli 2 units with the chlorine atoms placed above the edges of an octahedron x of platinum atoms. This structure is reminiscent of the tantalum(II) and molybdenum(II) The structure of PdCl 2 halide complex ions and is a further example of a metal cluster compound. The complexes of palladium(II) and platinum(II) are abundant and include all common ligands. Some examples have been given in Chapter 13 (see Fig. 13.18). Palladium(II) complexes are a little weaker in bonding and react rather more rapidly than the platinum(II) complexes, but are otherwise very similar. The commonest donor atoms are nitrogen (in amines, N0 2 ), cyanide, the heavier halogens and phosphorus, arsenic and sulfur. The affinity for F and 0 donors is much lower, but the stability of Pt(II) is underlined by the isolation from nitric acid of Pt(N0 3 ) 4  $^{\sim}$  where the nitrate groups are bonded through a single 0 forming a square-planar Pt0 4 coordination shell. Another example is provided by the planar PtH 4 ~ ion, a red-violet compound synthesized by the action of NaH on Pt under hydrogen. This is a further case of the polyhydride ions remarked on in earlier sections. While Pt(NH 3 ) 4 + ions are colourless in solution and PtCl 4 ~ is red, the salt [Pt(NH 3 ) 4 ] [PtCl 4 ] —named Magnus's green salt—is strongly coloured. The square-planar units stack, alternate cation and anión, directly above each other in the crystal with a Pt-Pt distance of 325pm. Similar species with small ligands which allow short Pt-Pt distances are also abnormally coloured, betokening a metal-metal interaction in the crystal. Such species have aroused interest as possible 'one-dimensional

conductors'. If some electrons are removed, as in the partly oxidized compound K 2 Pt(CN) 4 .0.3Br, the crystals become strongly conducting but only in the direction parallel to the Pt chains. A further interesting square-planar platinum(II) compound is Zeise's salt, one of the first organometallic compounds (see Fig. 16.5a). Similar ethylene complexes are formed with a variety of other ligands and for Pd as well. The dimeric species [C 2 H 4 PdCl 2 ] 2 rapidly gives CH 3 CHO and Pd in water. When linked with CuCl 2 to reoxidize the Pd, this becomes the basis of the Wacker process for converting ethylene to acetaldehyde: C 2 H 4 + PdCl 2 + 3H 2 0 -> Pd + CH 3 CHO + 2H 3 0 + + 2C1~ Pd + 2CuCl 2 -> PdCl 2 + 2CuCl 2CuCl + 2H 3 0 + 4- 2Cr + ±0 2 -> 2CuCl 2 + 3H 2 0 which adds up to C 2 H 4 4- ¿0 2 —≫• CH 3 CHO. The process is viable as the reaction between Pd and CuCl 2 is quantitative and efficient, so only low Pd concentrations are required. One or two examples do exist of coordination numbers other than four in the II complexes: Pd(diars) 2 Cl + for example is a trigonal pyramid and Pt(NO)ClS~ is octahedral (though the latter might be formulated as an N0~ compound of Pt IV rather than as the NO + compound of Pt 11 ). The SnCl^ complexes also provide examples. Platinum(II) forms a square-planar ion PtCl 2 (SnCl 3 ) 2 ~ (as does ruthenium) but it also gives the ion Pt(SnCl 3 )i~ which has a trigonal bipyramidal PtSn 5 skeleton. This species reacts with hydrogen under pressure to form the hydride ion HPt(SnCl 3 ) 4 ~. Palladium forms the ion PdCl(SnCl 3 )ర", but it is not yet known if this is a monomer or forms a chloride-bridged dimer which would be square-planar around the palladium. Such compounds are commonly precipitated as salts of (b> cP

FIG. 15.3 0 Some platinum clusters, (a) The basic building

unit of [Pt 3 (CO) 6 ] n (known for n up to 12), (b) the Pt 4 (CO) 5

skeleton of [(R 3 P)Pt] 4 (CO) 5 very large cations (like Ph 4 As + ) from acid chloride solutions containing palladium, or platinum, and tin. Compounds with analogous M-Ge bonds, such as (R 3 P) 2 M(GePh3)2, are also well known. The I state is uncommon and the established examples are M-M bonded dimers. This probably occurs in the reported [Pd 2 (CN) 6 ] 4 ~ and has been found crystallographically in [(Me 3 P) 3 Pd-Pd(PMe3) 3 ] 2+ . The structure shows a square-planar arrangement around each Pd, with the two planes mutually perpendicular. On heating to 100°C, a Me group cleaves from a phosphane and the Pd(II) complex [(Me 3 P) 3 PdMe] + is formed. Platinum (I) is found in the Pt-Pt bonded carbonyl anión dimer, [PtQ 2 (CO)]|~, again with square-planar coordination. In the 0 state, there are no stable carbonyls analogous to Ni(CO) 4 , though M(CO} n species are formed in low-temperature matrix studies. The isoelectronic M(CN) 4 ~ ions, and M(PF 3 ) 4 species, do exist and CO-containing molecules occur such as Pt(CO) n (PR 3 ) 4 \_ n (n = ∖, 2). There are also reports of Pt(NH 3 ) 5 and Pt(en) 2 analogous to the iridium compounds. It has also been shown that the phosphane complexes, (Ph 3 P) 4 Pt and (Ph 3 P) 3 Pt, are derivatives of Pt<sup>°</sup> rather than hydrides of higher states as originally reported. The structure of Pt(PPh 3 ) 3 has been shown to contain the planar PtP 3 group. A plane trigonal unit, PdH 3 , is found in the unusual species NaBaPdH 3 formulated as a Pd(0) complex hydride. The N a + H distance is short, suggesting further interactions (compare Section 9.4 for the unusual metallic hydride formed by palladium). Platinum forms a number of irregular clusters containing carbonyls. The family of polymetallic 2-carbonyl anions of the general type, [Pt 3 (CO) 6 ]n~, are built up of the basic unit shown in Fig. 15.30a. The Pt 3 triangles stack up above each other in twisted trigonal prisms, and species with n up to 12 have been characterized. The cluster of Fig. 15.30b is found in Pt 4 (PR 3 ) 4 (CO) 5 . The four Pt atoms, each with a terminal PR 3 , form a tetrahedron which has five out of the six edges bridged by CO groups. See also Section 16.8. 15.9 Silver, 4d 10 5s 1 , and gold 7 5o 1 °6s 1

Reasons for this were discussed in the copper

section (Section 14.9). The major part of silver chemistry is that of the d 10 state, Ag(I). Gold is most often found in Au (III) square-planar complexes, but tjiere are also a variety of Au (I) compounds, mostly complexes. Simple compounds of gold rieadily give the element, and silver is also reduced to the element fairly readily. These elements differ quite widely in their chemistries, and also differ from copper which occurs in the II state. The elements are found uncombined and in sulfide and arsenide ores. They may be recovered as cyanide complexes which are reduced to the metal, in aqueous solution, by the use of zinc. Gold is inert to oxygen and most reagents but dissolves in HC1/HN0 3 mixture (aqua regia) and reacts with halogens. Silver is less reactive than copper and is similar to gold, except that it is also attacked by sulfur and hydrogen sulfide. It is easiest to treat the two elements separately as there is little resemblance in their chemistries. 15.9.1 Silver There are a limited number of Ag m compounds; however, these are of potential interest because silver (III) is

isoelectronic with copper(III) (d 8 ), and because of the occurrence of both copper(II) and copper(III) in superconducting oxides (Section 16.10) it has been proposed that silver(II)-silver(III) fluorides might also show superconductivity. Oxidation in basic solutions gives [Ag(I0 0 ) 2 ] 7 ~ or [Ag(TeO 6 ) 2 ] 9 ~, and copper (III) compounds are obtained similarly. Fluorination of a mixture of alkali and silver halides gives M I AgF 4 , and red, diamagnetic AgF 3 may be precipitated by addition of a fluoro Lewis acid to AgFj solutions in anhydrous HF: AgF4 + L -\* AgF 3 + LF(examples of L include BF 3 ,PFs or AsFs) SILVER, 4d 5s , AND GOLD, 5d 6s 383

A highly important application of Ag(l) salts is in

photography. The basic process is the activation

by light of Ag centres in the AgBr film, and these

nucleate the formation of Ag metal particles

when reduction (development) occurs. The

unreacted salt is removed (fixing) by forming

soluble Ag + complexes, typically sulfur species.

Colour photography is based on the same

general process with the interposition of dyes

to filter out the three primary colours. The square-planar AgF 4 also reacts with the silver(II) ion AgF + , to give the maroon mixedoxidation state compounds Ag n Ag in F 5 which, with AgF 3 gives Ag n Ag 2 n F 8 . This latter compound is also formed by the thermal decomposition of AgF 3 . Solvated silver (III) is an extremely powerful oxidizing agent, even more powerful than krypton(II). Electrolytic oxidation gives Ag 2 0 3 which has the same structure as Au 2 0 3 , i.e. squareplanar MO 4 units linked by shared corners into a network. A similar oxidation in base yielded square-planar [Ag(OH) 4 ]~. The mixed Ag(II)-Ag(III) oxide, Ag 3 0 4 , has also been isolated from anodic oxidation work. All silver (III) compounds are strongly oxidizing. When Ag 2 0 is oxidized by persulfate, black AgO is obtained. This is a well-defined compound which is strongly oxidizing. It is diamagnetic, which excludes its being an Ag 11 compound which would contain the paramagnetic d 9 configuration. A neutron diffraction study has shown the existence of two

units in the lattice, linear 0-Ag-O and square-planar Ag0 4 groups. This strongly suggests a formulation as Ag I Ag III 0 2 . The square-planar configuration is expected for the d 8 Ag 111 while the linear one is common for d 10 as in Ag 1 (compare Ag 1 with Cu 1 or Au 1 which both show linear configurations and compare the III state with Au m ). AgO is stable to heat up to 100°C and it dissolves in acids, giving a mixture of Ag + and Ag 2+ in solution and evolving oxygen. Reaction of C1 2 with CsAgCl 2 gives the analogous mixed-oxidation chloride Cs 2 Ag I Ag III Cl 6 . The structure shows square-planar Ag m (Ag-Cl = 221 pm) and linear Ag 1 (Ag-Cl = 227pm). The only simple compound of silver(II) is the fluoride, AgF 2 , which is formed from the action of fluorine on silver or AgF. It is a strong oxidizing or fluorinating agent and can be used in reversible fluorinating systems in a similar way to CoF 3 . AgF 2 occurs in two forms: Ag I Ag III F 4 is a disproportionated, high-temperature form, while Ag n F 2 is a nondisproportionated low-temperature form, which has a blue colour. The square-planar AgF 4 ~ ion is also known. Salts containing the AgF + ion are well known, such as AgF[BF 4], which has an infinite linear chain -Ag-F-Ag-F-Ag-F-. Silver ions of the II state can exist in solution but only transiently. They are produced by ozone on Ag + in perchloric acid. The potential for Ag 2+ + e -» Ag + has been measured as 2.00 V in 4M perchloric acid. This makes Ag 2+ a much more powerful oxidizing agent than permanganate or eerie. Silver also gives a number of complexes in the II state. These are usually square-planar and paramagnetic corresponding to the d 9 state, and known structures, for example, of Agpy 4 + , are isomorphous with the Cu 11 analogues. Other examples include the cations Ag(dipy) 2 + and Ag(phen) 2 + . These cations are stable in the presence of nonreducing anions such as nitrate, perchlorate or persulfate. The interesting species Ag(MF 6 ) 2 (M = Nb or Ta) consists of a central AgF 6 octahedron sharing three cis F with MF 6 octahedra. The AgF 6 octahedron has two long and four short Ag-F bonds consistent with d 9 Ag(II). The normal oxidation state of silver is Ag 1 and the chemistry of this state is already familiar, for example from the precipitation reactions of Ag + in qualitative analysis. Salts are colourless (except for anión effects) and generally insoluble apart from the nitrate, perchlorate and fluoride Structures are usually similar to those of the alkali metal equivalents, for example the silver halides have the sodium chloride structure. As discussed in Chapter 5, their lattice energies are higher because the Ag + ion is more polarizable, hence the lower solubilities. Silver (I) forms a wide variety of complexes. With ligands which do not

Ti-bond, the most common coordination is linear, 2-coordination as in AgfNFyJ, while 7c-bonding ligands give both 2- and 4-coordinate complexes and 3-coordination is found for some strongly Ti-bonding ligands such as phosphanes. A number of very interesting complexes of silver (I) (and other late transition metals) with alkyl halides have been described recently, as detailed in the review given in Appendix A. Solvents such as dichloromethane and 1,2-dichloroethane are often used in synthetic inorganic chemistry because of their noncoordinating nature. However, the recent isolation of complexes of the type [Ag(CH 2 Cl 2 )(OTeF 5 )] and [AgN0 3 (CH 2 I 2 )], containing coordinated alkyl halides, clearly points to the term 'noncoordinating' now being of limited relevance. The isolation of such complexes is even more remarkable given that the silver (I) ion is a very powerful halide-abstracting group and the isolated halocarbon complexes may therefore be thought of, in some respects, as 'frozen intermediates' in the abstraction process. CHAPTER 15

The reader is referred to Sections 17.7.3 and

17.9.4 for further chemistry involving the OTeF 5

group. It is noteworthy that ions containing the poorly coordinating OTeF 5 group have been successfully employed in the isolation of all of these unusual halocarbon silver species, and this suggests that a range of other novel complexes should be accessible using this type of group. A formal 1/2 oxidation state is found in Ag 2 F. This has a layer lattice of the anti-Cd! 2 type and the Ag-Ag distance is similar to that in silver metal, which accounts for the low formal oxidation state. The properties are metallic. 15.9.2 Gold The highest oxidation state found for gold is the V state, which has the d 6 configuration. Thus Au(V) corresponds to Pt(IV). Powerful oxidation of AuF 3 with F 2 and XeF 2 gives AuF^ as the Xe 2 F+ 1 salt (compare Section 17.9). The AuF^ ion is a slightly distorted octahedron linked by long weak Au-F- • -Xe bonds to the two Xe atoms of the Xe 2 F+ 1 ion. Other cations, including the larger alkali metals and Oj, stabilize the AuF¿ ion. The KrF 2 AuF 5 species has a stronger bridge and is best seen as FKr-FAuF 5 with a more covalent interaction. AuF 5 is formed by gentle heating of the krypton compound. The pentafluoride is extremely reactive and a violent fluorinating agent. It decomposes to AuF 3 and F 2 at 200°C and forms HAuF 6 which melts at 88°C. Among unusual adducts are BrF 5 .AuF 5 which is oxidized by KrF 2 to BrF 7 .AuF 5 although free BrF 7 does not

exist (Section 17.8). Gold (III) is the most common oxidation state of gold in compounds. The interrelations are illustrated in Fig. 15.31 starting off from the solution in aqua regia. The simple compounds readily revert to the element but the complexes are more stable. Square-planar 4-coordination is the most common shape. AuCl 3 and AuBr 3 form planar bridged dimers (as R 2 AuX below with R = X) while AuF 3 forms a polymer made up of as-bridged AuF 4 units i.e. (AuF 2 F 2 /2)/ï. There is evidence for a few 6-coordinate complexes such as AuBr¿~. Examples of the tendency to 4-coordination are provided by the alkyls such as R 2 AuX. These contain a Au-C bonds which are among the most stable metal-carbon bonds in the transition block. The halides have dimeric structures: aqua regia . « , MCI 1 1 A \_ , Au − ^ AuCI 3 < HAuCI 4 heat∖ /heat AuCI heat chloro-auric acid Ix- Au(OH) 3 Au 2 O 3 ~Au(OH)i in solution ~ Au 2 O + A u square-planar complexes FiG. 15.31 Reactions of gold(lll) While, when X = CN, tetrameric structures are found: R 2 Au N C AuR 2 C N R 2 Au - N AuR 2 CH 3 (a) R 2 P" /a > Au Cl Au Cl H 2 R 2 K AuCl X DD 1| I"1 2 -Au-X H 2 R 2 f^ ">R 2 vW CI C I

FIG. 15.3 2 Transformation of the R 2 P-CH 2 -PR2 bridged digold

compound. The short 'bite' of the bidentate phosphane holds

the two Au atoms close together in a rigid conformation.

(a) Two gold(l) centres linked through the diphosphane.

(b) Oxidation forms the Au-Au bond giving gold(ll). (c) Further

oxidation gives two gold(lll) centers linked through the

diphosphane Formai Au(II) results from Au-Au bonding in the same way as Pt(III) in the last section (see Fig. 15.32). Ligands with two donor atoms close together, such as Ph 2 PCH 2 PPh 2 bridge two Au atoms holding them close together. Then stepwise oxidation by successive additions of halogen converts the Au from (I) through (II) with the Au-Au bond to (III). However, relatively few examples of gold(II) complexes have been prepared, and good o donors and n acceptors (such as dithiolate ligands) are required to stabilize the mononuclear, paramagnetic (d 9 ) gold(II) centre. The Au 2+ ion has recently been generated in a solid matrix by heating gold (III) fluorosulfate, Au(OS0 2 F) 3 , or in solution by the reduction of the same compound with gold metal in HOSO 2 F solution. Gold (I) is less stable but forms the simple halides and Au 2 0. Aul and AuCl have similar chain structures Y X / \ 7 ^x/^ XA \ /AU Complexes are usually linear, e.g. [AuX 2 ]~ (X = halogen, CN, etc.) or R 3 PAuX. X includes CH 3 as well as halides, etc. The R 3 PAu~ group itself forms a range of complexes, often of high coordination number, for example R 3 PAuV(CO) 6 or (R 3 PAu) 3 Re(CO) 4 . The long-known carbonyl Au(CO)Cl can now be readily made and is a valuable source of Au (I) complexes since the CO is very weakly bonded. Planar 3-coordinate Au (I) is found in (R 3 P) 2 AuCl and [(R 3 P) 3 Au] + . Gold(I)-sulfur compounds are of interest as photosensitizers of silver halide layers in photography. The hydrogensulfido complex [Au(SH) 2 ]~ has recently been prepared. It is suggested that this species is responsible for the transport of considerable quantities of gold in hydrothermal ore solutions. Au has a relatively high electron affinity (compare Table 2.9) and Au(-I) has the d 10 s 2 configuration which is fairly stable as found in Hg(0) (compare relativistic effects, Section 16.13). A very striking consequence is to have evidence for the Au∼ ion. The first indications appeared half a century ago, particularly the observation that CsAu has relatively little metallic character and is best formulated as a salt, Cs + Au~, containing the auride Au~ anión, rather than as an alloy. In line with this the compound crystallizes in the caesium chloride structure, rather than the more densely close-packed structures which are usually adopted by metals. However, there has been recent discussion as to the relative contributions of ionic and covalent character in the bonding in CsAu and an equal contribution from both of these bonding types is currently the most favoured opinion. A range of other derivatives containing anionic gold has been prepared in liquid ammonia or ethylenediamine (compare Section 6.7), and isolated in complexes with various large cations, especially (crypt)M + . The solid-state mixed-metal oxide derivative Cs 3 AuO has been prepared by reaction of Cs 2 O with CsAu and this compound also contains anionic gold. A related nitride auride, Ca 3 AuN, has also been described. 15.10 The zinc Group The zinc Group does not fit the general picture of the transition Groups as developed in the last two chapters. It shares with beryllium the property of belonging to one block of the Periodic Table and having many of the properties characteristic of another. In this case, the three elements of this Group resemble the three heavy elements of the boron Group. The elements, zinc, cadmium and mercury, in this Group have the outer electronic configuration d 10 s 2 and have the common oxidation state of II, corresponding to the loss of the two s electrons. In addition, mercury shows a well-established I state and cadmium and zinc form

analogous but very unstable I compounds. Thus the heaviest element is more stable than the lighter ones in a low oxidation state, a characteristic of the main Groups. However, a recent theoretical study has suggested that HgF 4 should be thermodynamically stable or, at worst, only slightly endothermic with respect to gas-phase HgF 2 and fluorine,

The radii also reflect this transitional character.

Shannon crystal radii for M(ll) are (pm)

Coordination no.

Zinc

Cadmium

Mercury 4 6 8 74 88 104 92 109 124 110 116 128

The significant increases between successive

Group members for the 4-coordinate radii is like

that found for a main Group while the pattern of

changes in 8-coordination is that typical of a

transition Group. (See also relativistic effects,

Section 16.13).

Mercury and many of its compounds are very

poisonous and, as mercury has a relatively high

vapour pressure at room temperature, mercury

surfaces should always be kept covered to avoid

vaporization. whereas CdF 4 and particularly ZnF 4 are much less likely to be stable entities. It was suggested that a relativistic de stabilization of the Hg(II)-F bonds, rather than a stabilization of HgF 4 , is the reason for this and that the use of powerful fluorinating agents, such as KrF 2 , might be suitable for the oxidative fluorination of HgF 2 to HgF 4 . The M n /M redox potentials show a large difference between Cd and Hg which can be ascribed in part to the higher solvation energy of Cd 2+ , which is an effect of smaller size. The potential values for M 2+ + 2e^M are: 2n = -0.762 V, Cd = -0.402 V, Hg = 0.854 V These values show the relatively high electronegativity of zinc and cadmium and reflect the reducing power of these elements. By contrast, mercury is unreactive and 'noble'. The elements are all readily accessible as they occur in concentrated ores and are easily extracted. Zinc and cadmium are formed by heating the oxides with carbon and distilling out the metal (boiling points are 90°C for zinc and 767°C for cadmium). Mercury(II) oxide is decomposed by heating alone, without any reducing agent, at about 500°C, and the mercury distils out (b.p. = 357°C). Mercury is the lowest melting metal with a melting point of -39°C, while zinc and cadmium melt at about 420°C and 320°C respectively. Mercury is monatomic in the vapour, like the rare gases.

Though the existence of the dimeric form of the

mercury(1) state is without doubt, there is now

also some evidence for the monomeric ion,

Hg + , both in solution and in solids. 15.10.1. The I state and subvalent compounds In the I state, mercury exists as the dimeric ion, Hg 2 + . This has been demonstrated by a number of independent lines of evidence: (i) The Raman spectrum of aqueous mercurous nitrate shows an absorption attributed to the Hg-Hg stretching vibration. (ii) The crystal structures of a large number of mercury(I) salts show the existence of discrete Hg 2 units. The structure of Hg 2 Cl 2 (Fig. 15.33) shows the presence of linear Cl-Hg-Hg-Cl units, but there are also longer Hg- • -Cl interactions which make the structure more complex. The stable organo-derivative RHgHgR [R=(Me 3 SiMe 2 Si) 3 Si], however, has a discrete molecular structure, and confirms the existence of a linear Si-HgHg-Si group. (iii) All mercury(I) compounds are diamagnetic, whereas an Hg + ion would have one unpaired electron. (iv) E.m.f. measurements on concentration cells of mercurous salts show that two electrons are associated with the mercurous ion. For example, the e.m.f. of the cell: mercury(I) mercury(I) Hg nitrate in (0.05moir 1 ) nitrate in (0.005molr 1 ) Hg O.lmoir 1 HN0 3 O.lmoir 1 HNO 3 was found to be 0.029 V at 25°C. Now£ = ^In(ci)/(c 2 ), where the concentrations are c\ and c 2 , n is the number of electrons, and the other constants have their usual significance. If values are put in for the constants and conversion to logarithms to the base ten is carried out, the equation becomes E = (0.059/n) log(0.05/0.005): hence 7 7 = 2 . (v) Conductivities and equilibrium constants also fit for a

dimeric ion of double charge and not for Hg + . The redox potentials involving mercury (I) are Hg 2+ + 2e- -> 2Hg (liquid) E = 0.789 V 2Hg 2+ + 2e~ -> Hg2+ E = 0.920 V It follows that, for the disproportionation reaction: Hg + Hg 2 + ^Hg2+ 387

#### FIG. 15.33 The

Hg 2 CI 2 Q Hg O Cl crystal structure of mercurous chloride, the potential is E = 0.131 V. Then, as E = (RT/nF) In K, where K is the equilibrium constant for the reaction: ^=[(Hg 2+ ]/[(Hg 2+ )] = about 170 In other words, in a solution of a mercury(I) compound there is rather more than \% mercury(II) in equilibrium. Thus, if another reactant is present which either forms an insoluble mercury(II) salt or a stable complex, the mercury(II) ions in equilibrium are removed and the disproportionation goes to completion. If OH is added to a solution of Hg 2+ , a grey precipitate of HgO mixed with Hg is formed. Similarly, sulflde precipitates HgS, and CN" ions give a precipitate of mercury and the undissociated cyanide of mercury(II), Hg(CN) 2 . The existence of this disproportionation reaction means that a number of mercury(I) compounds, such as the sulflde, cyanide or oxide, do not exist. The main compounds of mercury(I) are the halides and a number of salts. Hg 2 F 2 is unstable to water giving HF and HgO plus Hg. The other halides are very insoluble. Mercurous nitrate and perchlorate are soluble and give the insoluble halides, sulfate, acetate and other salts by double decomposition reactions. The nitrate and perchlorate are isolated as hydrates which contain the hydrated ion [H 2 0-Hg-Hg-H 2 0] 2+ . A three-atom chain exists in Hg 3 (AlCl 4 ) 2 where the basic structure is a Z-shaped molecule with Cl bridging between approximately tetrahedral A1C1 4 units and approximately linear Hg-Hg-Hg chains. In the reaction with fluoro-arsenic or antimony species, a number of poly-mercury ions result. For example, 3Hg + 3AsF 5 -> Hg 3 (AsF 6 ) 2 + AsF 3 4Hg + 3AsF 5 -\* Hg 4 (AsF 6 ) 2 + AsF 3 OHg + 3AsF 5 -> [Hg 2 . 85 AsF4 + AsF 3 (reaction in 802). The crystal structures show a linear symmetric Hg§ + ion with Hg-Hg = 255.2 pm. In Hg4 + , the structure is centro-symmetric and nearly linear with angle 176°: Hg<sup>Hg</sup>-<sup>Hg</sup>-Hg

#### AMALGAMS

The solution of a metal in mercury is given the

specific name amalgam (an old alchemical

term). For most metals, relatively dilute solu tions are liquid, and thus useful for reactions by providing a fresh surface. For example, many reductions are conveniently carried out by shaking the reagents in solution with 5% sodium amalgam. Amalgams are also used for depositing a surface film, e.g. in gilding, when the mercury is removed by evaporation - though the toxicity of mercury vapour makes this procedure dangerous.

Amalgam is thus a specific term for alloys

containing mercury. Infinite chains are found in [Hg 2 . 85 AsF 6 ]^ which contains chains of Hg atoms passing in two directions at right angles through a lattice of octahedral AsF¿~ ions. The average Hg-Hg distance is 264 pm. Similar mercury chains are found where the As is replaced by Nb or Hf, but such compounds change on standing to give golden crystals which contain planes of close-packed Hg atoms separated by layers of MF^ ions. Alkali metals dissolve in mercury to form amalgams and clusters of mercury atoms have been identified in the solids isolated from such amalgams. All these clusters involve formal oxidation states for mercury of around I. CsHg, KHg and Na 3 Hg 2 phases have all been shown to contain rectangular Hg 4 clusters. Even more striking is Rbi 5 Hgi 6 which contains slightly distorted Hg 4 squares and Hg 8 cubes (angles, 86-94°; Hg-Hg distances, 294-298 pm, except for two edges of the square at 304 pm). A parallel is to be drawn with the gold clusters discussed in Section 16.8. Mercury(II) and (I) carbonyl cations have been isolated in liquid antimony fluoride from Hg 2+ and CO at 100°C. The [Hg(CO) 2 ] 2+ and [Hg 2 (CO) 2 ] 2+ ions were isolated as the [Sb 2 Fn]~ salts, following a similar preparation of the analogous [Au(CO) 2] + cation. While neutral binary carbonyls are not known for the heavy elements to the right of the d block (compare Section 16.2), reasonably stable M-CO species have now been isolated as ions, or in presence of additional ligands, for most of these elements. The existence of a cadmium (I) ion, Cd 2 + , has been

conclusively proved in a molten halide system, CdAlCl 4 is obtained as a yellow solid and shown to be Cd 2+ (AlCl 4 ) 2 ". This reacts violently with water to give cadmium metal and Cd 2+ in solution. Cd 1 may also exist in the deep red melts of Cd in cadmium(II) halides. A recent report indicates that zinc (I), Zn 2+ , exists under similar conditions. 15.10.2 The II state The most stable state for all three elements is the II state. In this, zinc and cadmium resemble magnesium and many of the compounds are isomorphous. Mercury(II) compounds are less ionic and its complexes are markedly more stable than those of zinc and cadmium. All three elements resemble the transition elements more than the main Group elements in forming a large variety of complexes. The halides of all three elements are known. All the fluorides, MF 2 , are ionic with melting points above 640°C. HgF 2 crystallizes in the fluorite lattice and is decomposed in contact with water. The structures of ZnF 2 and CdF 2 are unknown: these compounds are stable to water and are poorly soluble, due both to the high lattice energy and to the small tendency of the fluorides to form complex ions in solution. In this the zinc and cadmium fluorides resemble the alkaline earth fluorides. The chlorides, bromides and iodides of zinc and cadmium are also ionic, although polarization effects are apparent and they crystallize in layer lattices. The structures are approximately close-packed arrays of the anions with Zn 2+ in tetrahedral sites in the zinc halides while, in the cadmium halides, Cd 2+ ions occupy octahedral sites. The zinc and cadmium halides have lower melting points than the fluorides and are ten to thirty times more soluble in water. This is due, not only to lower lattice energies, but also to the ready formation of complex ions in solution. A variety of species result, especially in the case of cadmium halides. Thus a O.Smoir 1 solution of CdBr 2 contains Cd 2+ and Br~ ions and, in addition, CdBr + , CdBr 2 , CdBr^" and CdBr|~ species, the most abundant being CdBr + , CdBr 2 and Br~ (these species are probably hydrated). Hydrolysis also occurs and species such as Cd(OH)X are observed. The tetrahalides, ZnX 2 ~ and CdX 2 ~, may be precipitated from solutions of the halides in excess halide by large cations. These are tetrahedral ions, as are all 4coordinated species in this group. By contrast, HgCl 2 , HgBr 2 and HgI 2 are covalent solids melting and boiling in the range 250°C-350°C. HgCl 2 is a molecular solid with two Hg-Cl bonds of 225 pm and the next shortest Hg-Cl distance equal to 334 pm, so that there is little interaction between the mercury atom and these external chlorines. In the bromide and iodide, layer lattices are formed, but in the bromide, two Hg-Br distances are much shorter (248 pm) than the rest (323 pm)
so that this is a distorted molecular lattice. HgI 2 forms a layer lattice in which there are HgI 4 tetrahedra with the Hg-I distance equal to 278pm. In the gas phase, the mercury halogen distances in the isolated HgX 2 molecules are, for X = C1, 228pm; X = Br, 240pm; X = I, 275pm. Thus the Hg-Cl distances are the same in the solid and gas, underlining the molecular form of the solid. The Hg-Br distance is a little longer in the solid, while the Hg-I distance is markedly longer in the solid, showing the increasing departure from a purely molecular solid on passing from the chloride to the iodide. Mercury also forms halogen complexes, and the same species are found for mercury as for cadmium. The stability constants for the mercury complexes are much higher than those for the zinc and cadmium species. Halo-mercury ions are found, e.g. (Hgl) + which exists as infinite chains, with I Hgl angles near linear and HglHg angles around 90°. In presence of a large cation, the HgCli" ion may be isolated, whose shape is a trigonal bipyramid with short axial Hg-Cl distances of 233 pm and long Hg-Cl equatorial distances of 303 pm. This can be seen as a linear Cl-Hg-Cl unit weakly coordinated by three further Cr ions.

THE ACTION OF CRYPTAND 222 ON MERCURIC HALIDES

The strongly coordinating ligand, cryptand 222 (see Such an experiment could be extensively devel

Fig. 10.6b and box in Section 10.6) has an interesting oped. For example, a cryptate with S donor atoms in

effect on mercury halides. Part of the mercury is coordiplace of the O would bond even more strongly to Hg

nated as the very large cation, [Hg(crypt 222)] 2+ and (compare Table 13.14), possibly leading to sequestra

this stabilizes complex anions [Hg 2 X 6 ] 2  $^{\sim}$  and even tion of a higher proportion of Hg as cations and

[Hg 3 I 8 ] 3 ~. The anión structures are based on tetraheopening up possibilities of more complex iodo

dral HgX 4 units with halogen bridges. mercury anions. 389 O Cd O Se

FIG. 15.34 The structure of the Cd 4 Sei 0 skeleton of the

[Cd 4 (SeR)i0] 2 ~ ion & C d o s

FIG. 15.3 5 The Cdi 0 S 20 skeleton of [S 4 Cdi 0 (SR) 16 1 4 The oxides are formed by direct combination. ZnO is white and turns yellow on heating. CdO is variable in colour from yellow to black. The colours in both cases are due to the formation of defect lattices, where ions are displaced from their equilibrium positions in the crystal lattices to leave vacancies. These may trap electrons whose transitions give rise to colours in the visible region. HgO is red or yellow, depending on the particle size. Zinc oxide and the hydroxide are amphoteric. Zn(OH) 2 is precipitated by the addition of OH~ to zinc solutions and dissolves in excess alkali. Cd(OH) 2 is precipitated similarly but is not amphoteric and remains insoluble in alkali. Mercury(II) hydroxide does not exist; the addition of alkali to mercuric solutions gives a precipitate of the yellow form of HgO. The elements all form insoluble sulfides and these are well known in qualitative analysis. ZnS is somewhat more soluble than CdS and HgS, and has to be precipitated in alkali rather than the acid conditions under which yellow CdS and black HgS precipitate. Most of the oxygen Group compounds of Zn, Cd and Hg have the metal in tetrahedral coordination in the zinc blende structure (see Fig. 5.1c) or in the related wurtzite structure (Fig. 5.4a). Both these are found for ZnS, with the wurtzite form the stable one at high temperatures. ZnO, ZnS, ZnTe, CdS and CdSe all occur in both the wurtzite and the zinc blende forms. ZnSe, CdTe, HgO, HgSe and HgTe are found in the zinc blende form only. HgS occurs in two forms, one is zinc blende and the other is a distorted NaCl lattice. The only other example of 6-coordination is CdO which forms a sodium chloride lattice. These structures again illustrate the strong tendency for these elements to form tetrahedral coordination. A growing range of sulfides and selenides of cadmium and zinc have been prepared which are polynuclear species containing segments of the tetrahedral ZnS structure. A small unit is seen in the Cd 4 Sei 0 skeleton of [(RSe) 6 (CdX) 4 ] 2 ~. Figure 15.34 shows the structure for X = SeR (note the SeR groups occupy both terminal and bridging positions). Other terminal groups, such as X halogen, are found, SR may replace SeR, and Zn may replace Cd. The basic skeleton is the same structure as P 4 Si 0 (Fig. 17.32b). In [S 4 Cd 10 (SR)i 6 ] 4 ", four of these units are fused together, see Fig. 15.35. Here, four of the S atoms are bonded only to Cd, six edges are bridged by SR, and the remaining SR are terminal on Cd. Again, Zn and Se analogues are known. Even larger polytetrahedral clusters are known, and the ultimate product of successive fusion is the sulflde. Such compounds may reflect the coordination of Cd in biomolecules. This formation of 4- and 6-coordinated species is also found in the complexes of these elements.

Zinc occurs largely in 4-coordination in complexes like Zn(CN) 4 ~ or Zn(NH 3 ) 2 Cl 2 and is also found in rather unstable 6-coordination, as in the hexahydrate and the hexammine, Zn(NH 3 )o + . Cadmium forms similar 4-coordinated complexes but is rather more stable than zinc in 6-coordination, due to the larger size. Mercury is commonly found in 4-coordination, though a few octahedral complexes such as Hg(en)i + are also found. All three elements are also found in linear 2-coordination especially in their organometallic compounds, and in the halides and similar compounds. The organic compounds R 2 M (M = Zn, Cd or Hg) are well known and mercury also forms RHgX compounds win halides. The so-called RZnX and RCdX species are, like the Grignard reagents (RMgX), more complex and their structures are not fully understood. They are polymeric with some evidence for MX 2 and MR 2 groups and are usually coordinated by the ether used in their preparation.

390 CHAPTER 15 THE ELEMENTS OF THE SECOND AND THIRD TRANSITION SERIES

## Problems

15.1 Carry out, for the transition elements of the second 15.3 Discuss the lanthanide contraction and its effects on and third series, the exercises given the Questions 14.1 transition metal chemistry. 15.4 Continue general surveys along the lines suggested

15.2 For each element of the second transition series in turn, for Chapter 14 Problems, e.g. Question 14.5. compare and contrast the chemistry with that of the other two elements in the same Group.

The best way to build up a clear picture of systematic chemisé Is to corroíate one Dodv of facts In as many ways as possibly look a! tie chemistry of

neighbouring elements, of othe? oxidation states of trt\$ dément of the same cf configuration, of lonsofthe same charge, etc. The problems below are

a guide to many similar on^s- whk^ you c§n <&\*«\$\$.

Many su«:h qu^ons can be derivkl, Surveys sliould stait with the first transite series In Chapter 14 and indite material from Chapters 9 mu 13,

Many should b& broached to the Heavy HaiBitlon oiements m Qiapler 15 f and often to the rest ol the Periodic Taole (see Chapters 10 to 12 and 17), The

special topics of Chapters 16 and £0 wB! afeo often l>e relevaot

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together with the comments on the different sections of this list.

16 CHAPTER 16 TRANSITION METALS: SELECTED TOPICS

Although sometimes written in a keto form, IVL M this bridging group has no ketonic properties. The bonding is best regarded as a three-centre overlap, similar to that of the B 3 faces in B 5 Hn (Fig. 9.12c).

(a) OC—M n Mn C O

(C) O C Co ' v A . In terms of electron counting, the bridging group contributes one electron to each metal, so two groups bridging two metal atoms have the same effect as if each was terminal on one metal. Thus the 18-electron rule does not allow us to distinguish bridging and nonbridging structures. This is well illustrated by the existence of the second isomer of cobalt carbonyl, Fig. 16.3c, which is in equilibrium with the bridged form in solution. Fe 2 (CO)9 has the structure shown in Fig. 16.3d, with three bridging CO groups placed symmetrically around the Fe-Fe bond. The Co 2 (CO) 8 form of Fig. 16.3b is. similar to this with one bridging CO removed. For Fe 2 (CO) 9, the electron count is 8 valency electrons plus 6 from three terminal CO groups plus 3 from three bridging CO groups plus 1 from the Fe-Fe bond making 18 at each iron atom. The presence of bridging carbonyls is clear from the infrared spectrum where the stretching frequencies of bridging groups are found at lower energies. Thus the terminal CO groups of Co 2 (CO) 8 give vibrations between 2028 and 2104 cm" 1 while the bridging modes are at 1898 and 1867 cm" 1 . The structures of the more complex carbonyls are built up in similar ways. For example, the M 3 (CO)i 2 species of the iron group have the structures of Fig. 16.4. Fe 3 (CO)i 2 involves bridging carbonyls and can be envisaged as Fe 2 (CO) 9 with one bridging CO replaced by a Fe(CO) 4 group. The Fe 3 skeleton is an isosceles triangle with the three Fe-Fe bonds indicated by the 18-electron rule. Ru 3 (CO) 12 and Os 3 (CO) 12 form equilateral triangles with no bridging carbonyls. A similar pattern is seen for the M 4 (CO) 12 species of the cobalt group, where the metal atoms form a tetrahedral cluster. For M = Co and Rh, the base triangle face consists of terminal (CO) 2 M units with a bridging CO along each edge

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and the apex is occupied by an M(CO) 3 group. For M = Ir, the structure is symmetric with four Ir(CO) 3 terminal units in a regular tetrahedron. It is found generally that bridging CO groups are commoner for the lighter elements. Hydrides with more complex structures are well known. Figure 16.5 shows some of the simpler examples. The edge-bridging hydrogens (as in Fig. 16.5c) are analogous to the B-H-B bridges in the boron hydrides (Fig. 9.10). In HFe 3 (CO)^, the H replaces one of the bridging CO groups of Fig. 16.4a. The simplest stable carbonyl of iridium is the tetranuclear species Ir 4 (CO) 12 which has all the CO in terminal positions and the Ir 4 core bonded together into a regular tetrahedron. The CO are oriented equally about the threefold axes so the overall symmetry is T d . The rhodium analogue has an alternative configuration where one Rh(CO) 3 unit is bonded to a triangle of three Rh(CO) 2 units with the last three CO edge-bridging this triangle (overall C 3v ). Co 4 (CO) 12 has the same sructure as the Rh carbonyl. Larger carbonyl clusters are a well-established and rapidly growing field which is included in Section 16.8.

FIG. 16.3 Binuclear carbonyls: (a) Mn 2 (CO)i 0 , (b) Co 2 (CO) 8 in

solid, (c) Co 2 (CO) 8 in solution, (d) Fe 2 (CO) 9 (CO) 4 °b, oc\* 8 (b) c g

FIG. 16.4 Structures of (a) Fe 3 (CO)i 2 , (b) Os 3 (CO) 12 16.2.4 Related species There are three other groups of compound which are closely related to the carbonyls. First the nitrosyls, where the NO group behaves similarly to CO but acts as a 3-electron donor. Thus Cr(NO) 4 is an 18-electron species and we can construct the isoelectronic series from this through Mn(CO) 3 (NO), Fe(CO) 2 (NO) 2 and Co(CO) 3 (NO) to Ni(CO) 4 , all of which are known. Further isoelectronic species of this type are Mn(CO)^ (obtained by Na/Hg reduction of Mn 2 (CO) 10 ) and Cr(CO) 4 (NO)~. Another ligand closely related to CO is PF 3 . Unlike organic phosphanes, such as P(CH 3 ) 3 , PF 3 is a poor a donor, as the electron density of the phosphorus lone pair is attracted by the electronegative fluorines. However, this same attraction makes the P a good n acceptor, using its empty 3d orbitals. As a result of these effects, PF 3 turns out to be a ligand very similar to CO, and PF 3 can replace terminal CO in most formulae, so we find Ni(PF 3 ) 4 , Fe(PF 3 ) 5 or Cr(PF 3 ) 6 for example. The properties of such species are very similar to those of the carbonyl analogues. It has been very striking to find that V(PF 3 ) 6 can be made and parallels the

carbonyl. It is a volatile paramagnetic molecule, corresponding to the same 17-electron count as the exceptional V(CO) 6, and it very readily forms the [V(PF 3 ) 6]~ anión, completing the 18 electrons. CHAPTER 16 399 (b) ^H\* § 8 (C) (CO) 4 Mn-- -Mn(CO) 4 H

FIG. 16.5 Some carbonyl hydride species: (a) HCr(CO)n

(b) H 2 W 2 (CO)Í|-, (c) H 3 Mn 3 (CO) 12 There is also a huge range of mixed-ligand compounds containing the carbonyl group. For example, we find the reaction (CH 3 ) 3 SnW(CO)- + NO+ -> (CH 3 ) 3 SnW(CO) 4 NO or the reaction of [(C 5 H 5 )Fe(CO)(PR 3 )I] to form other [(C 5 H 5 )Fe(CO)(PR 3 )X] species with halogens. Another class of related ligand, isoelectronic with carbon monoxide, is isocyanide (also known as isonitrile), RNC. One advantage of isocyanides over carbon monoxide as a ligand is that the steric and electronic properties of the former may be readily varied by changing the R group. Nevertheless, the number of isocyanide compounds is substantially less than> that of carbonyls. Analogues of carbonyl species such as Ni(CNR) 4 and Cr(CNR) 6 have been prepared, and in dinuclear and cluster compounds bridging isocyanides akin to bridging carbonyl ligands are also known. The isocyanide group is, in general, a better a donor than CO, and stabilizes complexes in higher oxidation states than does CO, for example the complex [Mn(CNR) 6 ] 2+ , which has no known carbonyl analogue. The isoelectronic cyanide ligand CNT, while invariably a carbon donor ligand, is a much poorer 7i-acceptor than CO or RNC and is best considered as a pseudohalide ligand. However, it is still useful to mention some related CO and CN~ complexes in the iron(II) system. Ferrocyanide (Section 14.6) is a very well-known and highly stable species, but the corresponding CO analogue, Fe(CO)o + , has only recently been prepared. Mixed CO-CN species are also known; Fe(CN) 5 (CO) 3 ~ was reported in the 19th century, while transFe(CN) 4 (CO)i" was only reported in 2001. The synthesis of the latter complex is surprisingly simple, involving the addition of 4 equivalents of NaCN to an aqueous solution of FeCl 2 under a CO atmosphere. 16.3 Metal-organic compounds

Many of the early attempts to make metal-organic

compounds were unsuccessful, and molecules

which were isolated, such as CH 3 CH 2 Mn(CO)5,

decomposed easily (in this case, at -30°C). The

discovery in 1951 of the very stable organome tallic compound, ferrocene (C 5 H 5 )2Fe, was thus of considerable moment. This was quickly found to have an unusual structure and the interest created led to a very rapid expansion of the organometallic field. The two chemists most involved in the organometallic revival, Fischer and Wilkinson, were jointly awarded the 1973

Nobel prize for this work. 16.3.1 Metal-carbon cr bonding The simplest system to consider is that of a metal bonded to a methyl group. Here, the only bonding interaction of any significance is a a bond using appropriate orbitals on M and CH 3 . Such bonds are very similar to the transition metal, M-H, bond and also to the relatively stable bonds to Main Group metals as in Sn(CH 3 ) 4 . One the whole, ^--bonded metalorganics are unstable. A number of simple compounds exist, notably Ti(CH 3 ) 4 , Nb(CH 3 ) 5 and W(CH 3) 0 with a few related species, which are well characterized but which decompose at or below normal temperatures, often violently. In the presence of other ligands, stability increases. Thus Ti(CH 3 ) 4 starts to decompose above -78°C but (CH 3 ) 2 TiCl 2 can be prepared at -20°C and diamine complexes are stable at 0°C. The higher alkyls are generally less stable, but aromatic derivatives are more stable than the methyls. It is instructive to examine the factors affecting that metal-carbon bond stability. A number are of importance: (1) the metal-carbon bond is probably relatively weak There is little quantitative data but we note the thermal instability and the fairly low force constants for the metal-carbon stretching vibration. (2) organic products of M-C cleavage are highly reactive Whether M-CH 3 cleaves to give methyl radicals or organic ions, these will react rapidly with the solvent or with each other. Contrast this with the cleavage of most metal-ligand bonds, e.g. M-OH 2 or M-C1, which give unreactive species such as H 2 0 or Cl~. (3) bonds formed by the organic cleavage products are relatively strong We expect to find bonds such as C-C, C-0, C-N, C-halogen, depending on the system. Thus we expect that, in a model reaction such as 2M-CH 3 -> H 3 C-CH 3 + M products (16.2) the forward reaction will be exothermic and thermodynamically preferred. Further, any equilibrium

Table 16. 2 Some examples of metal-carbon a bonds M-CH 3 > M - + -CH 3 (16.3) will be driven to the right as the • CH 3 will rapidly be removed by further reaction. However, even if compounds are thermodynamically unstable with respect to their decomposition products, their lifetime depends on the rate of the reaction, i.e. on their kinetic stability. Lifetimes range from the extremely short to the indefinitely long. The main factor affecting kinetic stability is the size of the energy input—the activation energy—required to get the molecule into a state where reactions such as Equations (16.2) or (16.3) occur. Such an input may involve bond weakening or breaking, formation of an intermediate, population of antibonding orbitals and so forth. If the required activation energy is large, the compound maybe stable indefinitely, even if the overall decomposition reaction has a strongly favourable free energy change. Similar comments apply to stability to other reactions such as oxidation or hydrolysis. With these comments in mind we can list some factors which will generally be expected to lead to relatively stable metal-carbon <r bonds. (1) If we make the reasonable assumption that population of the antibonding orbitals leads to bond breaking, any factor that increase the energy gap between the highest filled orbitals and the antibonding ones, will improve stability. Such factors are: (a) a d<sup>\*</sup> configuration—no electrons in the relatively high nonbonding orbitals such as t 2g in an octahedral complex. (b) in any other configuration, all factors increasing the ligand field M (compare Sections 13.3 to 13.5, and 13.12). (2) All factors which decrease the kinetic contribution such as: (a) steric hindrance from large ligands in higher coordination numbers. (b) substitution-inert configurations such as d 6 octahedral (see Section 13.9). (c) absence of low-energy pathways such as ^-elimination (in the interaction with /^-hydrogen below). (3) Factors which directly increase the metal-carbon bond strength. These include TI contributions to be M-C bond as discussed below. Of course, such contributions to stability do not necessarily have only one effect. Thus, TI bonding ligands L in L n M-(CH 3 )^ will increase A£ (see Ib) but will probably increase the metal-carbon bond energy as well. This energy, in turn, affects the stability through both its thermodynamic effect (decreasing the free energy change for the forward reaction of Equation (16.1)), and through its kinetic effect increasing the activation energy input for M-C bond cleavages as in Equation (16.2). Table 16.2 lists some examples of metal-carbon <r bonds, and it will be seen that the factors outlined above apply in most

cases. Note that there are many further examples with Ti-bonding ligands such as C 5 H 5 , CO, phosphanes, etc. The stability order C 6 H 5 > CH 3 > C 2 H 5 is accounted for by two features: (CH 3 ) 4 Ti CH 3 TiCl 3 Diamine Ti(CH 3) 4 (C 5 H 5)M(CO) 2 R M -Fe, Ru, Os (diphos)Ru(R)(H) (CH 3 ) 5 M M=Nb, Ta (C 5 H 5 ) 2 VR V(C Ó H 5 )^" RCo(CN)5~ RM(X) 2 (CO)(PR 3 ) 2 (M=Rh, Ir) (CH 3 ) 6 W (CH 3 ) 8 W 2 (C 5 H 5 )M(CO) 3 R M=Cr, Mo, W RCr(H 2 0)5 + (PR 3 ) 2 MR 2 (M=Ni, Pd, Pt) [(CH 3 ) 3 PtX] 4 RM(CO) 5 M=Mn, Te, Re (PR 3 )AuR (PR 3 )AuR 3 Notes (a) R = alkyl or aryl: stability usually decreases R = aryl > CH 3 > C 2 H 5 . (b) Stability increases down group e.g. M = Ni < Pd < Pt. (c) Note the common configurations are d or d 10 or the substitution-inert ones. METAL-ORGANIC COMPOUNDS 401 Interaction o f a meta l with a p-H atom (OC) 5 M H 3 C R f^U f\* L J = v-rM3 , V'6''5 M = Cr, C-Cr = 204 pm M = W, C-W = 205 pm (a) aromatic ligands (and unsaturated ones generally) allow for additional M-R n interactions between metal d orbitals and ligand n\* ones. Note, for example, that a metal-acetylide, M-C=CH, is isoelectronic with the carbonyls, M-C=0, discussed in the last section. Further, since the charge distribution is usually M Ô+ -C Ô ~, any organic ligand able to delocalize the negative charge should help stability. This applies to aromatic ligands, halogen-substituted ones, etc., culminating in the generally high stability of M-CF 3 groups. These, and related ligands, can be used to stabilize metal centres in high oxidation states. Thus, the copper(III) species, Cu(CF 3 )^, has been isolated as a stable colourless solid, which has a nearly square-planar structure, and the electron-withdrawing aryl group C 6 C1 5 forms the square-planar, d 7 , 15-electron nickel(III) complex Ni(C 6 Cl 5 )^. (b) It is commonly found that systems which do not contain H on the carbon /? to the metal atom are distinctly the more stable. Thus, in equivalent species, M-CH 3 , M-CH 2 C(R) 3 , M-CH 2 -Ar, M-CH 2 -SiR 3 or M-CH 2 -NR 2 are more stable than M-CH 2 CH 3 or M-CH 2 CHR 2 in general. This effect arises because the metal may interact with a /?-H atom. This provides an additional pathway for reaction (and the reverse reaction provides a synthesis). 16.3.2 Metal-carbon multiple bonding An interesting development has been the evidence that metal-carbon double and triple bonds may occur in the carbenes M = CR 2 , and carbynes AfeCR respectively. One of the first examples of a carbene was (CO) 5 WC(R)OMe whose crystal structure shows the CR(OMe) group completing an octahedron at W. The W-C bond length of 205 pm is greater than W-CO (190 pm). The bonding is formulated as (a) a W-C a bond plus (b) a n bond formed by a carbon p orbital overlapping with, say, d^ on W (z is W-CR 2 axis). As the d yz overlap would be identical,

there is cylindrical symmetry around the z axis and the CR 2 group is free to rotate. A range of metal-carbenes is now known. More recently a further family of compounds has been reported, the carbynes, with an M-CR unit. An example is I(CO) 4 WC(C 6 H 5 ). For this and related compounds, the structure is octahedral with the halogen trans to the CR and with the dimensions. ForR = CH 3 or C 6 H 5 and X = Br or I X(CO) 4 M-CR Cr-C = 169 pm W-C-190pm. The M-C-R angle is near 180° for R = CH 3 but about 170° for R = C 6 H 5 . The bonding is expressed as an overlap of p x and p y orbitals on C with metal d^ and d yz orbitals, in addition to the o component. Metal p x and p y may also contribute. Thus we have three classes of metal-carbon compound with the bonding along the M-C axis. These are analogues of C-C, C=C and C=C bonding respectively although the M-C, M=C and M=C systems are much weaker. A further, very widespread, class involving metal-carbon n bonding is that with unsaturated organic ligands bonding 'sideways-on' to the metal, and this is discussed in Section 16.4. The carbene or carbyne metal complexes essentially consist of a highly reactive organic fragment stabilized by coordination to the transition metal centre. They are examples of a general effect which is now very important in organometallic chemistry—that highly reactive species can be stabilized on coordination. A wide and diverse range of such stabilized reactive entities is now established, including highly strained cyclic alkynes, such as cyclobutyne and cyclohexyne, cyclobutadiene, benzyne and trimethylenemethane [C(CH 2 ) 3 ]. Inorganic entities are also stabilized, such as silylenes [R 2 Si] and the corresponding germylenes and stannylenes. A major reason for interest in metal-carbon bonded species comes from this stabilization, which applies to intermediates in many metal-catalysed organic reactions. Examples are the oxo-process (Section 14.7) the Monsanto acetic acid process (Section 15.7) or the Wacker process (Section 15.9). CHAPTER 16 M H 16.4 Ti-bonded cyclopentadienyls and related species

(a)

(b)

FIG. 16. 6 Zeise's salt anión, [PtCI 3 (C 2 H 4 )r: (a) structure,

(b) Pt ethylene bonding

SUBSTITUTED CYCLOPENTADIENYL LÍGANOS

Related substituted cyclopentadienyls are com monly used as n ligands, especially C 5 Me 5 (often labelled cp\*) where steric effects might be significant. One of the most substantial is C 5 Ph 5! 'supercp', in which the steric demand often forces alternative geometries. The first perfluorinated analogue, (C 5 F 5 )Ru(cp\*) was

recently discovered. A further large class of Ti-bonded transition metal complexes, which we can refer to only briefly here, is the group containing unsaturated organic molecules as ligands. The two classical examples we Zeise's salt, K[PtCl 3 (C 2 H 4 )].H 2 0, and ferrocene, Fe(C 5 H 5 ) 2 . In Zeise's salt, the three Cl atoms and the mid-point of the C=C bond form a square plane around the Pt atom, and the ethylene molecule lies perpendicular to this plane (Fig. 16.6a). The bonding is illustrated in Fig. 16.6b. As in the carbonyls, sigma donation is postulated from the ligand, this time from the filled C-C n orbital, and n donation from the metal into the ligand n\* orbital. In the ferrocene molecule the metal atom is sandwiched between the organic parts, C 5 H5-Fe-C 5 H5, and the planes of the organic rings are parallel (Fig. 16.7a). A very similar, situation is found for other aromatic systems, as in dibenzene chromium (Fig. 16.7b). An interesting extension of this class is the triple sandwich (Fig. 16.7c). Many more layers insuch sandwich complexes have been constructed of late and even a hexadecker sandwich has been described. This consists of five cobalt atoms and six cyclopentadienyl or boronsubstituted cyclopentadienyl ligands. Cyclopenl dienyl compounds are formed quite generally. Most transition metals form (CsHs) 2 M species. However, some, such as [(C 5 H 5 ) 2 Ti], are less simple than first thought, and all structurally characterized titanocenes have required the coordination of a neutral ligand such as CO or phosphanes to stabilize the d 2 metal centre. However, use of a substituted cyclopentadienyl ligand gives (C 5 Me 4 SiMe 2 Bu) 2 Ti, which has a ferrocene-like mononuclear structure with parallel cyclopentadienyl rings. The related ions, such as (C 5 H 5 )2Fe + , are also readily formed and redox relationships between ions and neutral species reflect the 18-electron rule. One interesting case is cp\* 2 Fe where the neutral compound is staggered, like the H analogue, but the cation is in the

eclipsed configuration. Molecules are found with one cp substituent together with other ligands, such as C 5 H 5 Mo(CO) 3 Cl, and the reader is referred to the review in Appendix A for a detailed account of compounds of this type. Dibenzene compounds are less widespread, but are typified by (C 6 H 6 ) 2 Cr, Fig. 16.7b, which has the Cr sandwiched between two parallel benzene rings. Other aromatic systems appear in similar compounds including the cation of cycloheptatriene (C 7 H 7 ) + and the dianion of cyclobutadiene (C 4 H 4 ) 2  $^{\sim}.$  The latter system has long appeared as a hypothetical aromatic system with no evidence of its actual occurrence. The parent hydride is still unknown, but the substituted molecule with four phenyl or methyl groups in place of the hydrogens has been attached to a nickel atom, as in the compound shown in Fig. 16.8. The four-membered ring is planar and the aromatic electrons appear to be fully delocalized. A very wide range of other aromatic systems containing heteroatoms has also been complexed to transition metals in a nmanner. Examples include pyridine (C 5 H 5 N), phosphabenzene (C 5 H 5 P) and the cyclic P 5 ligand analogous to cyclopentadienyl which is described in more detail in Section 18.3.1. The bonding in these aromatic sandwich compounds may be described briefly. The basic bond in ferrocene is a single bond of n symmetry between the iron atom and each ring. This bond is formed by overlap of the d^ and d yz orbitals on the iron (the z axis is the molecular axis, and these two d orbitals are of equal energy) with that aromatic orbital on each ring which has one node passing across the ring. These two metal d orbitals and the two ring orbitals combine to give two bonding n orbitals, of equal energy, and two antibonding orbitals. Each of these orbitals is 'three-centred' on each ring and the iron atom. There are four electrons in ferrocene which fill the two bonding orbitals. In the corresponding cobalt and nickel compounds, the extra electrons enter the antibonding orbitals, making these compounds less stable and giving cobaltocene one unpaired electron and nickelocene two unpaired electrons (as there are two degenerate n\* orbitals). One component of the n bond is shown in Fig. 16.9. Other overlaps add smaller contributions to the bonding, but this is the main interaction. The basic feature is that there is a single metal-ring bond and the rings are aromatic, undergoing aromatic substitution and similar reactions. Analogous orbitals can be constructed for the species with other C n Enrings. (C)

FIG. 16.7 The structure of metal sandwich compounds:

(a) ferrocene, (C 5 H 5 ) 2 Fe, (b) dibenzene chromium, (C

## 6H6)2Cr,

(c) tris(cyclopentadienyl)dinickel cation (CsiyNKCsH-JNi (C 5 H 5 ) + Many compounds are known which contain both carbonyl and Ti-bonded organic ligands. The wide variety of types is illustrated by the species n-C 5 E 5 N[(CO) x (M = V, Nb, Ta, x = 4; M = Mn, Tc, Re, x = 3; M - Co, Rh, Ir, x = 2). The dimers [7i-C 5 H 5 M(COy 2 are found with M = Cr, Mo, Wand;c = 3 or with M = Fe, Ru, Osandx = 2, or with M = Ni, P tandA:=l . Mixed-metal species include 7r-C 5 H5(CO) 2 FeMo(CO) 3 (7r-C 5 H5) 7i-C 5 H 5 (CO) 3 MoMn(CO) 5 , and and other n ligands include, in addition to cyclopentadienyl, C 5 H 5 , the groups C 4 H 4 , C 6 H 6 or C 7 H 7 or derivatives of these. Just as C 5 H 5 may be regarded as contributing five electrons to the central atom, these latter groups contribute respectively four, six or seven electrons. Also well known are allyl derivatives like 7i-C 3 H 5 Mn(CO) 4 where the C 3 H 5 group contributes three electrons, and diene derivatives where the substituent contributes four electrons, as in 7r-C 6 H 8 Re(CO) 3 H. Boron hydride analogues of ferrocene exist. For example, the B 9 C 2 H^ ion, which presents an open face consisting of a pentagon of three boron and two carbon atoms, can replace the C 5 Es ions/Compounds (B 9 C 2 Hn)Fe(C 5 H 5 r and (B 9 C 2 Hn) 2 Fe 2  $^{\sim}$  are formed which are ferrocene analogues, and these are oxidizable to Fe(III) compounds, such as (B 9 C 2 H n ) 2 Fe<sup>~</sup>, which are analogues of the ferricinium ion. This and many other carborane ions have been shown to replace the cyclopentadienyl ion in a variety of other compounds such as the cobalticinium ion and (C 5 H 5 )Mn(CO)3. FIG. 16.9 One component of the principal ring-metal-ring bond in ferrocene. This figure shows the interaction between the ring orbitals and the d\* orbital of the iron (where the z axis is the ring-metal-ring axis). The ring-d yz -ring interaction is similar • Ni O CI O C FIG. 16.8 Di(tetramethylcyclobutadienylnickeldichloride), (C 4 Me 4 NiCl2)2 16.5 The organometallic chemistry of the lanthanides An organic chemistry of the lanthanides has developed steadily since the establishment in the 1950s of the cyclopentadienyl (C 5 H 5 )~ compounds formed by the reaction LnCl 3 + 3NaC 5 H 5 -> Ln(C 5 H 5 ) 3 + SNaCl Such species are known for all lanthanides, though the route to Eu(C 5 H 5 ) 3 had to be indirect to avoid reduction to the europium(II) species Eu(C 5 H 5 ) 2 . The compounds are air and moisture sensitive and all except Sc(C 5 H 5 ) 3 readily form Ln(C 5 H 5 ) 3 D species with a range of donor molecules including D = NH 3 , THF, or R 3 P. The properties are basically ionic. The commonest structures have the C 5 H 5 rings and are planar with the

Ln 3+ ion lying above the centre with all five Ln-C distances equal. Further weaker interactions occur leading to polymeric units. Thus in Sc(C 5 H 5 ) 3 , one ring bridges two Sc atoms (in the 1,3 positions) giving a structure with long chains {-(CsHs^Sc-CsHs-ScfCsHs^-CsHs}^ In a similar way, the related Nd(C 5 H 4 Me) 3 is a tetramer in the solid. Closely related halides are also well known, e.g. LnX 3 + 2NaC 5 H 5 -> Ln(C 5 H 5 )2X or LnX 3 + Ln(C 5 H 5 ) 3 -> Ln(C 5 H 5 ) 2 X The structures are dimers with halogen bridges X (C 5 H 5 ) 2 Lr/ Ln(C 5 H 5 ) 2 yv and similar bridges form to other elements as: / Cl / \ ^ D (CsHsfcLn' |\_r " CI ^ D These halides maybe converted to other organometallics such as [(C 5 H 5 ) 2 LnR] x where R = H or an organic group. These compounds are usually dimers with electron deficient bridges: H R L/\n L /\n H L \ / Ln CI H tí (compare Figs 9.9 and 9.13). If R is a bulky group, such as C(CH 3 ) 3 or CH(SiMe 3 ) 2 , monomers are formed and these are also stabilized by donor molecules in (C 5 H 5 ) 2 LnR.D species. One interesting reaction is the abstraction of H from a C(CH 3 ) 3 substituent: 3(C 5 H 5 ) 2 Ln[C(CH 3 ) 3 ].THF + LiCl -> [Li(THF) 4 ] [{(C 5 H 5 ) 2 Ln} 3 (H) 3 Cl] where the anión has a core structure containing two types of bridging H. Bulky groups allow the isolation of species with direct Ln-C bonds of formulae LnR 3 or [LnR 4 ]~. The latter is stabilized by bulky cations such as (Li(THF) 4 ] + . Such compounds are found for ligands R = C 6 H 3 Me 2 , C(CH 3 ) 3, CH 2 SiMe 3, etc. These organolanthanide compounds are broadly parallel to those formed by the s elements, but they do allow a unique opportunity to assess steric effects. The Ln 3+ ions are large and compounds are clearly most stable when the ligands are very bulky. As the size of Ln 3+ varies in small steps from La 3+ to Lu 3+ , effects sensitive to size can be seen. Thus [Ln(C 6 H 3 Me 2) 4] [Li(THF) 4] could be isolated only for Ln = Yb or Lu. Similarly, [Ln{C(CH 3 ) 3 } 4 ] [Li(THF) 4 ] was formed for Ln = Sm, Er, Yb and La. Two interesting types of compound resulted when the ligands were made more bulky. First, the cyclooctatetrane (C 8 H 8 ~) sandwich compounds first found for the actinides (see U(C 8 H 8 ) 2 , Fig. 16.1 la) were paralleled in the species K(diglyme) + Ln(C 8 H) 2 . The crystal structure of the cerium compound shows Ce in the centre of a sandwich formed by parallel planar C 8 H 8 rings. Divalent lanthanide species M(C 8 H 8 ) and M(C 8 H 8 ) i~ are known for M = Yb, Eu and Sm. A second bulky ligand of interest is the C 5 Me^ ring. The stabilizes the Ln-R bond in a range of compounds (C 5 Me 5 ) 2 LnR, which are often dimeric (e.g. when R —H). In addition, the C 5 Me 5 group stabilizes divalent lanthanide compounds, such as in Sm(C 5 Me 5 ) 2 and its

solvated analogues: SmI 2 .THF + C 5 Me 5 K [(C 5 Me 5 )(THF) 2 SmI] C 5 Me 5 K (C 5 Me 5 ) 2 Sm (C 5 Me 5 ) 2 Sm(THF) 2 H 3 C

(a) CI

(b) CI X = CH or N

FIG. 16.1 0 Tr-arene complexes of the lanthanide elements:

(a) (7i-C 6 Me6)Sni(AICl4)3, (b) (7i-arene) 2 Ln (arène = tri methyl

or tri-f-butyl benzene or tri-f-butyl pyridine) In (C 5 Me 5 ) 2 Sm(THF) 2 , the coordination around Sm is roughly tetrahedral. When the THF molecules are removed, the structure remains bent with the ring-Sm-ring angle = 140°. Similarly, in (C 5 Me 5 ) 2 Yb, the angle = 158°. The unsubstituted compound Sm(C 5 H 5 )2 is also known. (C 5 Me 5 ) 2 Sm reacts with Ag + BPhJ in toluene to give the unsolvated cation [(C 5 Me 5 ) 2 Sm] + BPh4~, and the analogous Nd and Tm complexes have been prepared by reaction of the allyl complexes (C 5 Me 5 )2Ln(CH 2 CHCH 2 ) with [Et 3 NH] + BPh4. [(C 5 Me 5 ) 2 \_ Ln] + BPh4 (M = Sm, Nd) react with C 5 Me 5 K to give (C 5 Me 5 ) 3 Sm and (C 5 Me 5 ) 2 Nd. Complexes of the type Ln(C 5 Me 5 ) 3 were thought to be too sterically crowded to exist, but in 1991 the first complex of this type, Sm(C 5 Me 5 )3 was prepared by reaction of Sm(C 5 Me 5 ) 2 with cyclooctatetraene (C 8 H 8 ). Other routes to Sm(C 5 Me 5 )3 have since been reported, and Nd(C 5 Me 5 ) 3 is also known. Whereas the predominant oxidation state for organic derivatives of the lanthanides is the trivalent state (with the exceptions caused by the stability of the f<sup>°</sup>, f 7 or f 14 configurations, typified by Eu (II), Ce (IV), etc.), there is a developing chemistry of zero-valent organometallic compounds of the lanthanides. In an attempt to prepare the first example of a zero-valent sandwich complex Sm(p-C 6 Me ó ) 2 , analogous to dibenzene chromium (Fig. 16.7b), the reaction of SmCl 3 , Al, A1C1 3 and C ó Me ó was found to give the Sm(III) complex (7r-C 6 Me 6 )Sm(AlCl 4 ) 3 , Fig. 16.10a. The synthesis of zero-valent 7i-arene complexes was eventually achieved by employing the technique of metal vapour synthesis in which metal atoms (from a heated filament) are co-condensed with the organic molecule of interest at low temperature. By this method a number of zero-valent 7i-sandwich complexes have been synthesized from 1,3,5-tri-f-butyl benzene, and 2,4,6,-tri-f-butyl pyridine, such as the complexes shown in Fig. 16.1 Ob. Organolanthanide chemistry presents

interesting parallels with the chemistry of the s elements and B or Al species, a way of undertaking detailed study of steric effects, and a number of unusual species not found elsewhere in the Periodic Table. 16.6 Actinide organometallic chemistry (b) Fe(CO) 3 -CU (c)

FIG. 16.1 1 The coordination modes of cyclooctatetraene: (a)

as a planar dianion in uranocene, U(C 8 H 8 ) 2 (i.e. octahapto),

(b) as a delocalized diene (tetrahapto) in (C 8 H 8)Fe(CO)3, and

(c) as four alkenes (dihapto) in the [(C 8 H 8 )RhCI] 2 dimeric

complex Interest in the organometallic chemistry of the actinides is relatively recent. The larger size gives a preference for higher coordination and the main examples are formed by the IV and III states. The cp 4 E molecules are formed by Th, Pa, U and Np and the centroids of the four rings are arranged tetrahedrally around E. As well as cp and cp\*, a variety of cyclopentadienyls form similar compounds. Th and U also form cp 3 ER and cp 3 EX compounds in the IV state. In these molecules electron transfer from E into the ring n orbitals is relatively unimportant in the bonding and the main interaction is donation from ring n into the 6d and 5f orbitals. Both are significant, but the f contribution is weaker as the orbitals are large and dispersed. There are similar cp 2 EX 2 and cp 2 ER 2 species but these are less common. In oxidation state III all the actinides from Th to Cf have been shown to form cp 3 E, again with a variety of cp analogues. The centroids are arranged in a plane triangle around E. Cp 3 Cm and cp 3 Cf are the only well-characterized organometallic compounds of these elements. In a benzene Ti-complex, (C 6 Me 6 )U(BH 4) 3, the ring is planar and the centre, together with the three borohydrides, gives a tetrahedral array at U. The U-B distance indicates U(^-H) 3 BH coordination through three bridging hydrogens. While the carbonyl chemistry of the actinides is not well developed, we note the isolation and characterization (by single-crystal X-ray diffraction) of the uranium carbonyl complex, cp3\*U(CO) (where cp\*\* is the bulky tetramethyl-substituted ring, C 5 Me 4 H). The CO and the three ring centres lie tetrahedrally around U. The U-CO bonding (compare Section 16.2.2) consists of a donation by CO into the 6d^ 2 orbital on the U and backdonation from U 5f orbitals into the CO n\* orbitals. A further effect of the large size is the ability to

stabilize a larger ring system. There was great interest in the discovery, in 1968, of uranocene, U(C 8 H 8 ) 2 , which has two planar 8-membered rings forming a sandwich structure analogous to ferrocene (Fig. 16.11a). Similar E(C 8 H 8 ) 2 compounds were soon reported for Sc and other f elements including Th, Pa, Np and Pu. In contrast, the cyclooctatetraene dianion prefers alternative coordination modes to transition metals, as illustrated in Figs 16.lib and c. The E(C 8 H 8 ) 2 species are very sensitive to oxygen and water but have now been made with a wide range of substituted rings. Half-sandwiches, such as Th(C 8 H 8 )Cl 2 (THF) 2 , are also found. Simple alkyls and aryls are rare, though the anión [ThMe 7 ] 3 ~ has been stabilized with a complex cation and Th(CH 2 Ph) 4 is also relatively stable. E-alkyl bonds are more stable in the presence of n ligands as noted above. 16.7 Multiple metal-metal bonds 332pm 229pm • R e O C I FIG. 16.1 2 Structure of the Re 2 Cl|~ ion The discovery in 1964 of the ion Re 2 Cl 8 brought into the focus of chemists' attention the existence of metal-metal bonds of high bond order. The Re 2 Cl 8  $^{\sim}$ ion has the eclipsed structure shown in Fig. 16.12. There are two extraordinary features of this structure: the extremely short Re-Re distance of 224 pm (compare 274 pm in Re metal) and the eclipsed configuration which makes the CI-CI distance between opposite halves of the molecule markedly less than twice the Cl van der Waals' radius (compare Table 2.11). It was soon demonstrated that a wide range of similar rhenium (III) species existed, of general type Re 2 XS~ where X was a univalent anión, and with Re-Re distances in a very narrow range, around 222 pm. Such species often occurred with further ligands, such as H 2 0, on the Re atoms in the axial position trans to the Re-Re bond but this substitution had only a minor effect on the Re-Re distance. A further series of compounds with very short M-M bond lengths were those with carboxylic acid groups bridging the two metals, of the type Re 2 (0 2 CR)i + . Mixed species like Re 2 Cl 4 (0 2 CCH 3 ) 2 are also found. The dinuclear species bridged by four acetate groups, M 2 (0 2 CCH 3 ) 4 , was already well known e.g. for M = Cr (Fig. 14.20) or M = Cu (Fig. 14.33). The molybdenum acetate, Mo 2 (0 2 CCH 3 ) 4 , has a short Mo-Mo distance of 211 pm, thus extending the class of multiple metal-metal bonds to Mo (II). The chromium compound has Cr-Cr of 238 pm (compare the metal, 258 pm) so it also belongs to this class. (Note that not all dimeric acetates show multiple bonds—the copper compound has a long Cu-Cu distance of 265 pm compared with 256 pm in the metal). The Cr 2 molecule has been identified in the gas phase from photolysis of Cr(CO) 0 and has an extremely short Cr-Cr bond length of 168 pm, which was discussed as a sextuple

bond. A further group of short metal-metal bonded species was found for neutral compounds M 2 X 6 where M = Mo (III) or W(III) and X = halide, NR^, OR", etc. Other formulae include the rather rare M-C a bond in W 2 (CH 3 )g~, bridging carbonate or sulfate analogs to the acetates, e.g. Re 2 (S0 4 ) 4 , and the cyclooctatetraene derivatives M 2 (C 8 H 8 ) 3 (M = Cr or W) with one bridging C 8 H 8 group (Fig. 16.13a). The first stable technetium species was Tc 2 (O 2 CCMe 3 ) 4 Cl 2 (Fig. 16.13b) which shows axial ligands and seems to require them for stability as Tc 2 Cl 8  $\sim$  is unstable. (a) Me 3 C FIG. 16.1 3 Unusual metal-metal bonding: (a) W 2 (C 8 H 8 ) 3 , (b) Te 2 (02CCMe3) 4 Cl2 CMe 3 CME 3

TABLE 16.3 Species with multiple metal-metal bonds V 2 [C 6 H 3 (OMe) 2 ] 4 Cr 2 [0 2 CR] 4 Cr 2 [C 8 H 8 ] 3 Cr 2 [C 5 Me 5 (CO) 2 ] 2 Mo 2 [0 2 CR] 4 ) Mo 2 X^~ J Mo 2 [S0 4 ]^ Mo 2 X 6 W 2 [Cl 3 Me 5 J 4 W 2 [C 8 H 8 ] 3 W 2 X 6 Te 2 [0 2 CCMe 3 ] 4 Cl 2 Te 2 Cl 3 8 Re 2 X 2 8 Re 2 [0 2 CR]^ + Re 2 0\*Ru 2 (0 2 CR) 4 Cl Rh 2 (0 2 CCH 3 ) 4 M-M distance (pm) 220 185-254 228 209-214 216 220-224 226 238 227-230 219 212 220-224 223 226 228 239 Bond order 3 4 3 4 3.5 3 4 4 3 4 3.5 4 3 3 4 (3 unpaired electrons) 3? Comments Few examples Many examples: very variable bond length Many examples including mixed species and extra D Compare 211 pm in Mo 2 [S0 4 ] 4 ~ Many examples including extra D Also W 2 Me^~ Many examples including extra D Tc 2 Clg~ very unstable Many examples including mixed species and extra D In La 4 Re 2 Oio Chain structure linked through anión Cl" Compare 246-255 for Rh=Rh and 280 ±15 for Rh-Rh Notes (1) Where a range is given, this shows the commonest bond lengths. Unusual species greatly widen the range, e.g. 218 pm in Re 2 Meg~ and 226 pm in Re 2 Cl 5 (diphos)2. (2) X = halide, OR", NRi~ and other monovalent monodentate anions. O 2 CR = carboxylic anión or other bridging bidentate species. D = neutral donor such as H 2 0, R 3 N, R 3 P. (3) Multiple bonds are found in rather different types of compound, (a) For Fein [(C 4 R4) 2 Fe](¿í-CO) 3 and [(R 3 P) 3 Fe] 2 (^-H) 3 whichhaveFe-Fe = 218 pm and 234 pm respectively (bond order 3 postulated). (b) For Ir, in [(R 3 P) 2 (H)Ir] 2 (^-H) 3 f a triple bond is also postulated. (c) Long triple bonds are found for Cr, Mo, W in species of the type (C 5 H 5 )2M 2 (CO)4. While a multitude of homonuclear multiply bonded complexes are known, Table 16.3, compounds with two different metals are rare. Until recently, the only examples of such heteronuclear compounds contained two metals from the same Group of the Periodic Table, such as Cr-Mo or Mo-W dinuclear complexes. Only very recently, the dinuclear quadruply bonded complex [(TPP)MoRe(OEP)] + , containing

two metals from different Groups (Mo and Re), has been synthesized. In this complex, both metals are coordinated by macrocyclic porphyrin ligands; the porphyrin ligand on Mo is a tetraphenylporphyrin (TPP) Et Ph Et Et TPP OEP

(a) Re Re

(b) xory xory Re Re

(c)

FIG. 16.14 The quadruple bond in Re 2 Clg~: (a) a component,

(b) TI (one of the two components), (c) ô component

Double bonds are fairly widespread and we

quote just one type (C 5 H 5 )M:

found for a number of metals M (e.g. Fe, Rh)

and a range of bridging groups X and Y including

CO, NO, NR 2 and organic groups. while that on Re is an octaethylporphyrin (OEP); the two porphyrins differ in the positions and type of substituents on the macrocycle. 16.7.1 Bonding The unusual properties of Re 2 Cli~ were explained by Cotton by postulating a quadruple Re-Re bond, Fig. 16.14. If we consider the Re-Re axis asz, and x and y to lie along Re-Cl directions, then the square-planar ReCl 4 unit will be bonded using the Re s, p x , p y and d x 2\_ y2 orbitals. The Re-Re <j bond is then formed using the d Z 2 orbital, on each Re. (If we include p z contributions as well, a second orbital on each Re, pointing outwards along the z axis, is suitable for bonding the additional axial ligands.) The d^ and a yz orbitals on each Re may then overlap to give two Re-Re n bonds. This leaves the d^ orbital on each rhenium to form a 0 bond. Thus a bond of order 4 may be formulated with the occupancy o 2 n 4 d 2 . We see that the <5 component explains the eclipsed configuration (and indeed was proposed because of this configuration) whereas a pair of n bonds allows any configuration. The 0 component makes a relatively weak contribution to the total bond strength since the two nodal planes reduce the electron density (compare n bonds which are in turn weaker than a bonds—see Fig. 3.13). It has been estimated that the ô contribution is less than 15% of the total bond energy. Calculated stabilization energies in Mo 2 Cl8~ were approximately -7.3, -6.1 and -4.9 eV for a, n and ó electrons, respectively. If we take the Re(III) 2 Xg~ and the carboxylate species as bases, it will be clear that the corresponding Cr(II), Mo(II) or W(II) species M 2 Xs~ and M 2 (0 2 CR) 4 are isoelectronic and will also be formulated with a quadruple bond. If we then move to Mo(III) or W(III), and at the same time take two X~ ligands away, we leave enough electrons to form o 2 n 4 . Thus we obtain the well-represented M 2 X 6 class. As the triple bond does not impose barriers to rotation, these species are staggered in configuration like ethane. We can add a donor group (retaining the triple bond), as in Mo 2 (OR) 6 .2NHMe 2 , and find that the M 2 X 8 configuration is adopted with approximately planar M(OR) 3 (NHMe 2 ) units, but the two ends of the molecule are again staggered. A triple bond also results if 2 electrons are added to the quadruple bond since the lowest empty orbital is <5\*. Thus we get the o2 n 4 ô 2 ô\* 2 configuration for Re 2 Cl 4 (PEt 3 ) 4 (regard the 4P lone pairs as replacing 2C1~ lone pairs and 2C1 single electrons—hence the two additional electrons). Finally, if we remove one electron from the quadruple bond we get ff 2 n 2 o l f corresponding to a bond order of 3.5. Two pairs related in this way are Mo 2 (SO 4 ) 4 ~ with Mo 2 (SO 4 ) 4 ~ and the unstable Tc 2 Cli~ with Tc 2 Cli~. In most cases, oxidation causes structure change as in the reaction of Re 2 X1~ with halogens to form the face-sharing bisoctahedral structure of Re 2 X^~. Quite often, reactions of these multiply bonded species occur with little change to the M 2 unit. A striking case is the addition of axial donor groups: for example the Mo-Mo distance in Mo 2 [O 2 CCF 3 ] 4 is 208 pm and in (C 0 H 5 NMo) 2 [0 2 CCF 3 ] 4 it is 213 pm.'Some M 2 X 6 species undergo insertion reactions: W 2 (NMe 2 )6 + 6C0 2 -> W 2 [0 2 CNMe 2 ] 6 Mo 2 (NMe 2 ) 6 + 4C0 2 -> Mo 2 [(NMe 2 ) 2 (0 2 CNMe 2 ) 4 ] The substituted species have very similar M-M bond lengths but the M coordination number increases. For example, W 2 (0 2 CNMe 2 ) 0 has two bridging W-OC(NMe 2 )-OW units together, one bidentate and one monodentate ligand on each W, making W 5-coordinate to oxygens. These metal-metal bonds of high order complete a natural progression which starts from very weak interactions—e.g. Cr-Cr of 391 pm in Cr 2 Clg~ and the Cu 2 [0 2 CCH 3 ] 4 case mentioned above—through single bonds (compare Figs 16.3 and 16.4), and double bonds to these cases of order 3 to 4. The steps in bond order are not nearly as sharp as they are in Main Group chemistry (e.g. between C-N, C = N, and C=N) but the whole range of species represents a continuum of metal-metal interactions. 16.8 Transition metal clusters Many areas of interesting chemistry involve compounds where a number of metal atoms are bonded together directly and the M-M bonds are often supported by bridging ligands. If

we use a broad definition of a cluster as any species with more than two M atoms linked together, then we would include the compounds of Figs 15.25, 15.30, 16.4 and 16.5 as clusters. Such compounds represent only the tip of the iceberg of a large field of substantial current interest. Clusters are known under ambient conditions ranging in size from three to over a hundred metal atoms and an even larger variety has been detected by spectroscopic and other means. The development has stemmed partly from improved synthesis and characterization—in particular in the greatly increased accessibility and improved performance of X-ray crystallography. In addition, the work has been driven by the possibility of using soluble metal clusters in place of heterogeneous catalysis on metal surfaces. With the smaller clusters this idea largely failed, mainly because a group of a few metal atoms does not reproduce the properties of bulk metal or even of metal surfaces. However, the larger clusters which have become available more recently do begin to act as bulk metal and interesting developments can be expected. Thus, in a Pt 30 9 cluster, it was found that 147 core atoms do behave like bulk metal whereas the 13 core atoms in Au 55 still differ in charge density from the bulk. Work with clusters of this size is right at the limit of current techniques, falling within the limits in which X-ray crystallography and scanning electron microscopy are most effective (Section 7.11). Much work has been reported on smaller clusters, with intensive study of species containing from 4 to about 20 metal atoms. We will look briefly at three classes of these metal clusters. 16.8.1 Halide clusters We have already met a few examples of transition metal clusters in the M 6 X n species formed by Zr (Fig. 15.3), Nb and Ta (Fig. 15.9), or Mo and W (Fig. 15.19). Further halogenbridged clusters are reported, including [Ti ó C](¿¿-Cl 12 )Cl ó which resembles Fig. 15.9b but also contains a central C atom in an octahedral site. Extended halogen-bridged structures are known, including chains and sheets of linked octahedra, and this area extends into the layer and three-dimensional structures of the lower halides and oxides. An exotic example is [Y 16 Ru 4 I 2 o]n where a central tetrahedron of Ru atoms is sheathed by 16 Y which form fused octahedra containing Ru at the centre. The whole metal cluster is sheathed by Y-I bonds and the I atoms bridge to other clusters giving a three-dimensional network. However, a major focus in cluster work has been on species like the carbonyls which have no or few bridging groups and are clearly held together by M-M cluster bonding. 16.8.2 Carbonyl and related clusters To sample this extensive field of chemistry we look first at some moderate-sized clusters and then at a small selection of larger species.

In Table 16.1 we have noted the formation of M 4 (CO) 12 carbonyls by Co. Rh and Ir and there are a variety of related compounds such as [H 2 Ir 4 (CO) 10 ] 2  $^{\sim},$  Ru 2 Co 2 (CO)i 3 or [Fe 4 (CO)i 3 ] 2 ~ which all contain a tetrahedron of metal atoms with various combinations of terminal and bridging CO. In contrast, [HFe 4 C(CO) 12 ]~ and [Os 4 N(CO) 12 ]~ have a butterfly structure with two triangles sharing an edge (Fig. 16.15a). Similarly, Os 5 (CO)i 6 contains a trigonal bipyramidal Os 5 skeleton (Fig. 16.15b) while Os 5 C(CO)i 5 has a square pyramid of Os atoms (Fig. 16.15c). Many examples of octahedral clusters of metal atoms are known including [M 6 (CO) 16 ] [M = Co, Rh, Ir (Fig. 16.15d) with 2 terminal CO on each M and the remaining CO bridging], and [M 6 (CO)i 8 ] 2  $^{\sim}$  [M = Fe, Ru, Os (Fig. 16.15d) with 3 terminal CO on each M] and the similar [M 6 (CO)i 7 ] [with C at the centre of the octahedron]. Two octahedra joined by a RhRh(^ 2 -C0) 2 bridge occurs in [Rhi 2 (CO) 30 ] 2 ~. Interstitial atoms are now well established with B, C and N found in smaller clusters while larger units, such as C 2 or even C 3 , and heavier atoms like Si, Ge, Sn, P, As or Sb, are found interstitially in larger clusters. (a) (b ) (c )

FIG. 16.1 5 Some small cluster skeletons: (a) M 4 butterfly, (b) M 5 trigonal bipyramid, (c) M 5 square pyramid, (d) M 6 octahedron, also indicating a capping site for M 7( (e) M 6 capped trigonal

bipyramid Even interstitial H is now well established, usually in an octahedral site as in [HRu 6 (CO) 18 ]-. Rationalization of such variations has been approached by use of the 18-electron rule (see Section 16.2.1) or by an extension of SEP theory (compare Section 9.6). You can determine that the 18-electron rule works for the four- and five-metal examples above but fails for the six-metal ones. For example, the two Fe 4 species give electron counts of 60 for [Fe 4 (COh 3 ] 2  $^{\sim}$  and 62 for [HFe 4 C(CO) 12 ]  $^{\sim}.$  To achieve 4 x 18 = 72 electrons thus requires six Fe-Fe bonds in the former case and five in the latter. The tetrahedron allows 6 M-M bonds along the six edges, whereas the pair of triangles sharing one edge need only 5 M-M bonds. The cluster [Fe 6 (CO) 18 ] 2 ~, for example, has 86 electrons, compared with 108 required by the 18-electron rule which would require 11 M-M bonds. However, the octahedron has 12 edges (and the structure is fully symmetrical) so the idea of each metal being joined by a normal bond breaks down. To apply Wade's rules we note that the modification required is to count 12 electrons per metal atom for external bonding, in place of the 2 electrons per B atom in the boranes. The calculation of the number of skeletal electron pairs for [Fe ó (CO) 18 ] 2 ~, for example, then proceeds: from the 86 electrons subtract 6x 12 = 72 electrons for external bonding, leaving 7 SEP. Thus (compare Table 9.6) the expected structure is an octahedron. Note that in electron counting of these species atoms like C or N which are encapsulated are taken to add all their valency electrons to the count and to be incorporated in the skeletal bonding without requiring any specific allocation of electrons. A further example is the two Os 5 cases quoted above: Os 5 (CO) 16 5 Os valency electrons = 5 x 8 =40 16 CO contributing 2 electrons each = 32 less 12 electrons per Os = -60 giving 12 electrons or 6 SEP Thus the structure is the 5-vertex cluster, a trigonal bipyramid [Fig. 16.15b: all vertices are Os(CO) 3 apart from one equatorial Os(CO) 4 ]. Os 5 C(CO) 15 5 Os 40 electrons C 4 electrons 15 CO 30 electrons less 12 per Os - 60 electrons giving 7 SEP Thus the structure is an octahedron less one vertex, a square pyramid (Fig. 16.15c: all vertices are Os(CO) 3 and the C lying just below the base). (d) (e)

FIG. 16.1 7 Structure of the metal core of osmium atoms i

the giant cluster [Os 2 o(CO) 40 ] 2  $^{\sim}$ 

FIG. 16.1 8 The metal core of the cluster [Rri 13 (CO)2 4 H x ] (5  $^{\sim}$  x) The series [Os 6 (CO) 18 ] 2 , Os 7 (CO) 2 i and [Os 8 (CO) 22 ] 2 is interesting as the counts are each 7 SEP. Thus the expected structures are octahedra and the extra metal atoms in the two latter cases are in capping positions (compare Fig. 16.15d). A significant test case is Os 6 (CO) 18 . While there are a large number of octahedral M 6 complexes, this molecule is one of a few examples of the capped trigonal bipyramid (bicapped tetrahedron) shown in Fig. 16.15e with all vertices Os(CO) 3 . The electron count (48 + 36 less 6x 12) gives only 6 SEP, thus predicting a trigonal bipyramid with the extra atom taking up a capping position. Out of the large number of carbonyl clusters with 10 or more metal atoms we can look briefly at only one or two structural themes. Figure 16.16 shows the skeleton of the [H 5 Osio(CO) 24 ]~ ion and related clusters. The electron count gives 7 SEP so this is an octahedron with four caps. These are the outer apices in the figure and each is an Os(CO) 3 unit. All the rest are Os(CO) 2 units defining the octahedron. An alternative way of looking at this structure is as a large tetrahedron with atoms placed at the mid-points of each edge or, alternatively, built up of layers containing 1, 3 and 6 atoms. A big brother is known, [Os 20 (CO) 40 ] 2 ~ (Fig. 16.17), which is a giant tetrahedron containing layers of, successively, 1, 3, 6 and 10 atoms. In a rather similar way

[Ni 38 Pt ó (CO) 48 ] ó ~ is close to a giant octahedron with 10 atoms in each face (or layers of 1, 4, 9, 16, 9, 4 and 1 atoms). Such layers are in the positions corresponding to close-packing. A further family of structures can also be regarded as being built up from close-packed layers. The simplest example is [Rhi 3 (CO) 24 ] 5 ~ 7 Fig. 16.18, which has a central Rh inside a regular cluster— alternatively seen as close-packed layers of 3, 7 and 3 atoms. Related species also contain encapsulated H atoms. Larger clusters of this type are for example, a Rh 22 species with layers arranged 3, 6, 7, 3, [Pt 26 (CO) 32 ] 2 ~ with 7, 12, 7 layers and a Pt 38 species with 7, 12, 12, 7 layers. A further theme is stacked polygons. Compounds with up to five stacked triangles have been established and stacked squares or pentagons have also been found, along with a hexagonal prism. A particularly symmetric member of this family is [Pti 9 (CO) 22 ] 4 ~ which has D 5h symmetry and consists of three pentagonal bipyramids sharing apices (alternatively described as a 1, 5, 1, 5, 1, 5, 1 system). 16.8.3 Gold clusters Different structural features are seen in the rapidly developing field of gold clusters which often incorporate silver atoms also. Gold (I)-sulfur chemistry has yielded the complex ion [Aui 2 S 8 ] 4  $^{\sim}$ which has an unusual cubic structure in which the S atoms are at all the corners and the 12 Au atoms are in the centres of the edges. The structure is slightly distorted with angles at S in the range 87-93° and the Au atoms in essentially linear configuration, as preferred. The Au • • • Au distances are 318-335 pm which suggests a weak interaction (see Section 16.13 for discussions of Au- • -Au interactions). In lower formal oxidation states gold forms an extensive range of cluster compounds. In [Au 4 (PR 3 ) 4 ] 2+ gold .atoms, each with one terminal phosphane, form a regular tetrahedron with very short Au-Au edges. Short distances are also found, for example, in [Au 6 (PR 3 ) 6 ] 2+ which has formal oxidation state 0.33. The gold atoms, again each with one terminal phosphane, form an axially compressed octahedron. This form is paralleled in [Au 7 (PPh 3 ) 7 ] + in which the 7 Au form a pentagonal bipyramid with a short axial Au-Au distance. Further examples of the poly-gold clusters include [Au 9 L 8 ] 3+ , [Au n L 7 ] 3+ , [Aui 3 L 12 ] 3+ and related species where L includes phosphanes and halides. The Au 13 species has one Au atom at the centre of an Aui 2 icosahedron. The other two species also have a centred Au with the remaining atoms forming an incomplete icosahedron. Evidence has been presented for the much larger [Au 5 5(PPh 3 ) 12 Cl 6 ] cluster containing an inner Aui 3 icosahedron surrounded by an outer shell of Au, Au-P and Au-Cl units. Very large

mixed silver-gold clusters have also been found. A closely related pair are [Aui 3 Agi 2 (PR 3 h 2 Cl 7 ) 2+ and [Au 13 Agi 2 (PR 3 )i 0 Br 8 ) + (Fig. 16.19) whose structures consist of two icosahedra sharing

FIG. 16.1 6 The cubic close-packed metal core of [H 4 0si 0

(C0) 24 ] O Ag Au

FIG. 16.19 The metal core of the cluster [(R 3 P)ioAui 3 Ag 12 .

Br 8] + (R=p-tolyl)

The smallest colloid particles are some 10 times

the diameter of these large metal clusters and

contain 5000 to 20000 atoms. a vertex with a gold atom at the centre of each. An alternative description of this structure is as a succession of alternate pentagons and single atoms in an array: Ag, 5Au, Au, 5Ag, Au, 5Ag, Au, 5Au, Ag. The two structures differ in the relative orientations of the pentagons and in the distribution of the ligands. In the chloride ten of the phosphane ligands (R=para-Tol) bond to the Au atoms and two more to the two apical Ag. In the bromide the halogens bridge the two central Ag 5 pentagons and also bond to the terminal Ag. A number of larger clusters belong to this family, including [AuisAg^PPhsJ^Brn] 2 " and [Au22Ag24(PPh 3 )i 2 Cli2] whose structures are also based on icosahedra sharing vertices. These large and magnificent structures show how giant molecules can be assembled using clusters (in these cases the centred M 13 icosahedron) as the building blocks to form clusters of clusters. The L-Au(I) unit readily attaches to other metal clusters so that gold is incorporated in clusters with many metals. Examples are VAu 3 L 9 , containing a VAu 3 trigonal pyramid, and Fe 4 Au2(C)L 14 in which the 2 Au atoms occupy neighbouring positions in an octahedron enclosing the C. In such compounds L is generally CO or a phosphane, or similar ligands in combination. 16.8.4 Very large clusters The larger metal clusters quoted so far have reached a size where experimental problems arise in isolation and characterization. In particular, X-ray crystallography meets difficulties as the strong scattering from the metal core starts to swamp the picture. Thus, there are sometimes uncertainties about how many CO or other lighter groups are present. Despite this, compounds with around 40 metal atoms have been identified, such as [Pt 38 (CO) 44 ] 2 ~ which

contains five layers with, respectively 4, 9, 12, 9 and 4 Pt atoms in approximately square arrays. A mixed-metal example is [Ni 36 Pt 4 (CO) 45 ] ó "~ where a tetrahedron of Pt atoms is encapsulated in a truncated giant tetrahedron of Ni atoms (one size up from Fig. 16.17). One approach to systematic synthesis of larger clusters notes that the ratio of ligand to metal decreases as complexes get larger—e.g. 3 or 4 CO per M in M 3 , M 4 or M 6 species down to about 2 for Figs 16.17 and 16.18. Schmid used even lower MAigand ratios, and also bulkier ligands such as PPh 3 in place of CO, and isolated even larger clusters termed ligand-stabilized clusters. In this way, [Au 55 (PPh 3 ) 12 Cl ó ] was prepared which has been used as the model compound for investigating the onset of metallic properties (see Box). Larger, though less completely defined, clusters formed by this route include mixed-metal clusters containing silver and gold, a Pt 30 9 species, and palladium complexes with 500 to 2000 metal atoms. Working in the other direction, downwards in size from colloids, it is possible to probe the region between large clusters and metallic particles. Colloids such as palladium absorb CO readily and surface Pd-CO groups have been identified by infrared and 13 C nmr spectroscopy. From the cluster side, organic groups bonded to a metal atom in a cluster like Fig. 16.17 do interact with other metal atoms in the face and undergo unusual reactions. Such studies serve to clarify reactions on metal catalysts leading to novel or improved applications. Such studies have built up structures where some of the metal atoms have only other metal atoms as their nearest neighbours and the question arises, at what point do they start showing properties of bulk metals? Thus, in Fig. 16.18, the central Rh is surrounded by 12 Rh atoms in a (slightly expanded) close-packing array (compare Section 5.6). A similar configuration is found for each of the three central gold atoms of Fig. 16.19. In larger clusters, a group of metal atoms may be similarly surrounded such as the Pt 4 tetrahedron described above. Schmid's Au 55 cluster has an inner Au 13 icosahedron surrounded by an outer shell of Au, Au-P and Au-Cl units so the Au atom at the centre of the icosahedron is surrounded by a double shell of metal atoms. The largest synthesized clusters start to resemble metals, and it is expected that such materials will display interesting electronic properties. The diameters of these clusters are on the scale of nanometres (1.4 nm for the Au 55 core of the Schmid cluster) and are being studied as part of the current interest in 'nanomachines' and nanoscale electronics (see Box).

LIGAND-STABILIZED CLUSTERS, QUANTUM DOTS AND MOLECULAR WIRES

When does a metal cluster act like a metal? Studies in the last two decades clearly show that metal particles in the 1-4 nm size range are electronically character ized by quantum size effects—that is, instead of electrons being in conduction bands which are delocalized over the whole cluster in three dimensions (compare Section 5.6) they fall into discrete energy levels. This is a transitional region between the fully delocalized electrons in a metal, and the electrons in a molecule which occupy discrete energy levels. Particles showing such quantum size effects have been termed quantum dots and they show novel electronic proper ties which are of great interest in microelectronics. The ligand-stabilized clusters fall into this size range and the Au 55 cluster has been studied in detail. It turns out that not only are its two uppermost electrons trapped in the quantum box of the 55Au core, but that the diameter of the core plus ligands, equal to 2.1 nm, allows electrons in the first excited state to tunnel between clusters when they are held in contact. Exploitation of these properties depends on being able to order the clusters. A one-dimension ordering or 'molecular wire' can be achieved by adsorbing the

clusters onto an atomic step on a crystal plane. An alternative is to use nanopores in alumina as tubes and fill them with clusters—creating bundles of molecular wires. The formation of parallel tubes in A1 2 0 3 formed by anodizing aluminium is a wellunderstood process and experiments to fill 1-200 nm lengths show promise. Ordering in two or three dimensions is more difficult as the complexes precipitate as powders. Studies have explored bonding the complexes to metal or silica surfaces by substituting the phenyl groups of the PPh 3 with active groups, as in P-C 6 H 4 SC>3. Work in two- and three-dimensional ordering has also explored the use of 'spacers' created by using chains of different lengths and rigidities bonded to the phenyl groups to create bridges between clusters or to substrates. The chemistry, by providing flexibility in the size of the metal cluster and in the properties of the stabilizing ligands, creates a series of compounds which are valuable in the study of materials on the borderline between metals and molecules. Reference G. SCHMID, Journal of the Chemical Society, Dalton Transaction 1998, 1077-82. increasing numbers of metal atoms mononuclear dinuclear trinuclear hexanuclear polynuclear metal colloid particl e 16.9 Metal-dioxygen species Several areas of work have converged to create the current interest in species containing 0 2 groups bonded to metals. Compounds resulting from the action of hydrogen peroxide have long been of interest, e.g. in analysis— see Sections 14.2 to 14.4 for the Ti, V and Cr species as examples. Secondly, the reversible uptake of oxygen gas by haemoglobin (see Fig. 20.4) and other oxygen-carrying proteins has been shown to depend on dioxygenmetal coordination. Much work has gone into the study of such systems and into the syntheses of simpler model compounds which might aid understanding. A third area of interest lies in catalysis of oxidation by 0 2 : here the basic species is again likely to be an 0 2 M unit formed on the metal surface in the case of a heterogeneous catalyst or formed by homogeneous catalysts such as métallo-enzymes.

Table 16.4 M-0 and 0-0 bond lengths (pm) in peroxo M0 2

units Tl 145-46 185-89 Zr obs. Hf obs. V 144-47 187-88 Nb 148-51 197-204 Ta obs. Cr 140-46 181-92 Mo 138-55 191-97 W 150 193 Mn Tc obs. Re obs. Fe Ru obs. 05 obs. Co 142-45 187-90 Rh 142-47 202-03 Ir 130-52 200-07 Ni obs. Pd obs. Pt 145-51 201 (a) Upper value is range of O-O distances in the reported compounds and the lower value is the M-0 range. (b) Obs.=peroxo species observed but no structural data. There has been considerable debate about the formulation of metal-dioxygen species. First we recognize that it may be difficult to distinguish, let us say, M (I) plus neutral 0 2 from M (II) plus 0^ (superoxide) from M (III) plus 0 2 ~ (peroxide), since it may not be possible to determine the degree of electron transfer from M to the 0 2 species. An example is given by the cobalt species in Section 14.7.1, where green [(NH 3 ) 5 Co-0-OCo(NH 3 ) 5 ] 5+ was originally formulated as a superoxo species containing one Co(IV) atom. Secondly, the method of synthesis does not, as was thought, give any guidance. For example, direct addition of molecular 0 2 is found (Equation 16.4). [IrCl(CO)(PR 3 ) 2 ] + 0 2 -> [(0 2 )IrCl(CO)(PR 3 ) 2 ] but A is iridium(I) and B is best formulated as a peroxo complex of indium (III). Indeed, it has now been demonstrated that the same species results either by the action of 0 2 or by the traditional reaction of hydrogen peroxide in a number of cases such as Equation (16.5) [Co m (H 2 0)2(diars) 2 ] 3+ + H 2 O 2 [Co I (diars) 2 ] + + 0 2 ^[(0 2 )Co m (diars) 2 ] + (diars = bidentate arsane ligand, see Appendix B). (16.5) M (1) end-o n M (2) side-o n M M (3 a and b) bridged (4) double-bridged However, there is now sufficient evidence from molecular structure determinations to show that M-O 2 units exist as one or other of the forms (1) or (2) (see margin). There are also two bridged forms: 3 (a) where the M-O-O-M unit is all in one plane and 3(b) which is non-planar with a twist angle generally about 145° between the two MOO planes. Finally a double-bridged species has recently been reported. The side-on form (2) is by far the commonest, and the structures of about fifty species have been determined. The two M-0 distances are usually equal within experimental limits, and M-0 increases with metal size while 0-0 distances are relatively constant. Table 16.4 lists the ranges found. The 0-0 distances fall in the range 130-155 pm and 90% are between 140 and 152 pm, while the overall average is 146 pm (compare 149 pm in 0 2  $^{\sim}$  and 147 pm in H 2 0 2 ). The number of established end-on structures of type (1) is much smaller but these are characterized by much shorter 0-0 bond lengths (compare 0^ = 128 to 134 pm). This bond length evidence is supplemented by the 0-0 stretching frequencies, which have been assigned for a much larger number of complexes than have had crystal structures determined. Furthermore, when the M-O-O-M bridged structures are examined it is found that the values for the planar species (3a) fall into the same range as the end-on M0 2 species (1), while those for the non-planar species (3b) agree with the side-on MO 2 species (2). The values are summarized in Table 16.5. Z

Table 16.5 Parameters in metal-d ioxygen species

Bond type

End-on (1)

Side-on (2)

Planar bridge (3 a)

Twisted bridge (3b)

Double bridge (4) Metal(a] Fe(III), Co(III), Rh(III) Table 16.4 Co(III) Mn(III), Fe(III), Co(III), Rh(III), Mo (VI), Co (II)? V(IV) Average 0-0 distance (pm) 125 145 131 144 149 Average 0-0 frequency (cm" 1 ) (b) 1134 881 (3d elements) 872 (4d elements) 850 (5d elements) 1110 807

(a) Metal species forming this structure type.

(b) Stretching frequencies (cnT 1 ) of 0 2 = 1556 cm<sup>"</sup> 1 , CXT = 1145 cm~∖0l~ = 770 cnr Thus, apart from the double-bridge example, there are only two basic types of metaldioxygen species: (A) those with a shorter 0-0 distance and stretching frequency above 1075 cm" 1 . (B) those with a longer 0-0 distance and stretching frequency below 950 cm" 1 . Type A shows the end-on structure or the planar bridge while type B shows the side-on structure or twisted bridge. While there are a few marginal cases, most known species fall firmly into one or other class. The species of type A are formulated as superoxo compounds, formally derived from the superoxide ion 0<sup>^</sup>. The species of type B are peroxo-, based on the peroxide ion Q>\~. Bonding to the metal mainly involves the filled n\* orbitals (compare Section 3.4) of the dioxygen unit. These electrons are markedly stabilized by their delocalization into metal orbitals and the reduced n\* density in the 0 2 unit leads also to some stabilization of the 0-0 bond (seen especially in the slight shortening of the 0-0 bond and increase in stretching frequency for the peroxo-compounds). These descriptions for A and B are supported by a number of other physical properties and by theoretical analysis. 16.10 Compounds containing M-N 2 units and their relationship to nitrogen fixation There is considerable chemical interest in the activation of a molecule as stable and strongly bonded as N 2 , and in comparisons between complexes of N 2 and the isoelectronic species, especially CO and C\~. By studying metal-dinitrogen complexes we can begin to obtain an understanding of the fundamental chemical steps which occur during nitrogen fixation by the so-called nitrogenase enzymes. This is of great technological importance—much energy is utilized annually in synthesizing ammonia fertilizer from dinitrogen at high temperatures and pressures. If we can begin to understand the fundamental chemistry occurring in these enzymes we can design catalysts to synthesize ammonia under very mild (and hence

inexpensive) conditions. A discussion on the nature of the structures of the active sites of the nitrogenases is given in the section on bioinorganic chemistry in Chapter 20, together with some of the attempts at directly mimicking the complexes responsible for the nitrogen fixation process. In this section we look more closely at the interaction of the dinitrogen molecule with transition metal centres and what reactions the coordinated N 2 molecule undergoes, which is of relevance to the problem of nitrogen fixation. Of particular importance is the reduction of a coordinated N 2 molecule to reduced, but still metal-bonded, nitrogen-containing species and ultimately to the desired, fully reduced product-ammonia.

[Me 5 C 5 is the fully substituted analogue of

C 5 H 5 : the structures are probably 'bent sand

wiches' of the type found in (C 5 H 5 )2TaH3, see

Fig. 15.7). Ph Ti Ph f Bu(Ar)N Xx N f Bu(Ar) f Bu(Ar)N N'BiKAr ) ' ∖ N N f Bu(Ar)N ^^ V\*N f Bu(Ar) ' N Mo. V^N'BuíAr) x N f Bu(Ar)

FIG. 16.20 Cleavage of N 2 by a 3-coordinate molybdenum

complex (Ar = 3,5-dimethylprienyl) 16.10.1 Metal compounds with coordinated dinitrogen species There are two distinct classes of reaction which fix dinitrogen into other chemical compounds: (a) Under non-aqueous conditions and with powerful reducing agents, N 2 can be fixed in the form of air-sensitive and often poorly characterized materials which react with H 2 0 or other proton sources to yield NH 3 , or partly reduced species such as N 2 H 4 . Of course, the simplest species of this type, such as Li which forms Li 3 N with N 2 , have long been known (compare Section 10.5). More complex systems are illustrated by the titanium species discussed in Section 14.2. A number of similar systems are well established but all depend on active organometallics as the reducing agents. Thus these systems do not appear to provide a suitable route for industrial N 2 fixation, but they model the take-up of N 2 under very mild conditions and allow study of the steps of the subsequent conversion. Thus TiCl 3 and Mg react with N 2 at 25°C forming a species postulated as TiNMg 2 Cl 2 , via Ti 11 and subsequent reaction with Mg. Under even milder conditions, at -78°C, (Me 5 C 5 ) 2 Ti gives (Me 5 C 5 )TiN 2 which changes structure at -62°C and evolves N 2 quantitatively at 20°C. The two structures suggested contain N 2 respectively end-bonded and side-bonded to the

(Me 5 C 5 ) 2 Ti fragment. Other model reactions include the formation of N 2 H 4 from N 2 via Ti(OR) 2 polymer [R = (CH 3 ) 2 CH], and the ready formation of a substituted diimine complex (C 5 H 5 ) 2 Ti(N 2 Ph 2 ) perhaps with a sideways link as illustrated. The compound [Me 5 C 5 ZrN 2 ] 2 N 2 contains both linear Zr-N=N units (N=N of 112 pm) and bridging Zr-N=N-Zr (N=N of 118 pm). On addition of HC1, both N 2 and N 2 H 4 are evolved and tracer studies showed half the hydrazine nitrogen was from the terminal N 2 and half from the bridge. The intermediate (Me 5 C 5 ) 2 Zr(N 2 H) 2 was postulated. One recent development in this field is the 3-coordinate molybdenum complex Mo(NRAr) 3 (Ar = 3,5-dimethylphenyl; R = f-butyl), Fig. 16.20 which cleaves dinitrogen. The first and slowest step (which takes several days) involves the uptake of molecular N 2 and formation of a bridging N 2 intermediate. The second stage of the reaction, which is much more rapid (half-life about 30 minutes) involves cleavage of the N 2 group to give two molybdenum-nitrido complexes, containing Mo=N triple bonds. The Mo(NRAr) 3 complex also reacts with white phosphorus (P 4 ) to give the corresponding Mo=P complex. We may add to this class of reaction the work in aqueous systems which are a long way away from biological conditions of moderate pH and solution reactions. An example is provided by the observation that a coprecipitate in base of Mo(III-V) with 10% Ti(III) converts N 2 via N 2 H 2 to hydrazine, with the active species probably Mo (IV). This type of system may become important in larger-scale synthesis, as it is cheap and accessible, even though it does not model the natural fixation route. We note again the formation of hydrogenated N-N compounds. (b) In aqueous media, relatively stable complexes are formed, mainly by elements in the middle of the transition series especially in d 6 states. These contain N 2 as a ligand but the complexes are unreactive or release unchanged N 2 when attempts are made to reduce them under mild or moderate conditions. Thus these compounds allowed a detailed study of the modes of M-(N 2 ) bonding. The first of these compounds to be made was [Ru(NH 3 ) 5 N 2 ] 2+ (see Fig. 15.27). Many others are now known (see Table 16.6 for some examples). Common preparations involve strong reduction in presence of N 2 and other ligands, as in WC1 4 (PR 3 ) 2 + Na/Hg + N 2 -> W(N 2 ) 2 (PR 3 ) 4 or replacement of labile ligands, which often occurs reversibly under mild conditions. -H 2 0 Ru(NH 3 ) 5 (H 2 Or + + N 2 ^ Ru(NH 3 ) 5 (N 2 ) z CoH 3 (PR 3 ) 3 + N 2 ^ CoH(N 2 )(PR 3 ) 3 + H 2 CHAPTER 16

Table 16. 6 Some representative stable N 2 complexes Z M NH The coordinated diimine in (A) -NH 2

The coordinated hydrazid e ligan d in (B) Terminal N 2 (C 6 H 6 )Cr(CO) 2 N 2 P 4 M(N 2 ) 2 (C 5 H 5 )M(CO) 2 N 2 (C 5 H 5 )Re(CO)(N 2 ) 2 P 4 ReCl(N 2 ) P 3 M(H) 2 N 2 [(NH 3 ) 5 MN 2 ] 2+ P 3 (H)CoN 2 P 2 MC1(N 2) P 3 NiH(N 2 ) Bridging N 2 [(C 5 H 5 ) 2 Ti] 2 N 2 [(C 6 H 6 )PM] 2 N 2 [(NH 3 ) 5 M] 2 N 2 (P 3 Co) 2 N 2 [P 2 Ni] 2 N 2 M M M M M = Mo, W = Mn, Re = Fe, Ru, Os = Ru, Os = Rh, Ir Notes (1) PR 3 (phosphane) or 2x(diphosphane)=P. (2) All are d 0 except the compounds of Ti(d 3 ), Co(d 8 and d 9 ), Rh and Ir(d 8 ) and Ni(d 9 and d 10 ). A wide range of such coordinated dinitrogen compounds has been made, with various types of NN-M bonding, and differing stabilities. The next step in modelling fixation is to consider that it is unlikely that the naturally occurring reduction N 2 -> 2NH 3 is a direct one-step process. Instead, it seems probable that a number of intermediates follow the formation of the first complex, S-N 2 (5 = substrate: here the metal atom site of nitrogenase). A scheme which is consistent with most of the currently accepted observations is shown in Fig. 16.21. Here each addition step involves the supply of both H + and an electron, and the paths branch at some points. Thus, in addition to complexes containing bound N 2 in all its modes, work has also been carried out on diazenido (NNH), diazene or diimine (NHNH), hydrazido (NHNH 2 ), and hydrazine complexes, as well as single-nitrogen species containing M-N, M-NH and M-NH 2 groups. To illustrate this, we cite one series of experiments. The addition of H to N 2 bound to W has been established with reactions such as trans [W(N 2 ) 2 (diphos) 2 ] + 2HC1 -> [W(N 2 H 2 )Cl 2 (diphos) 2 ] + N 2 (A) The Mo complexes behave similarly, as does HBr (diphos is a bidentate ligand such as R 2 PCH 2 CH 2 PR 2 ). The complex (A) is 7-coordinate but will lose a halide ion (A) + BF 4 -> [W(N 2 H 2 )Cl(diphos) 2 ] + [BF4 ] + CF (B) Structural studies show that the N 2 H 2 group differs between (A) and (B). In (A), it behaves as a 2-electron donor—the unsymmetrically coordinated diimine HN = NH. S NH 2 -NH 2 -N 2 H 4 S-N=N ' S=N= N S NH 3 FIG. 16.2 1 The transformations involved in the conversion of substrate (S) bound dinitrogen into NH 3 or N 2 H 4 . Each step involves transfer of a proton and the corresponding electron H However, the loss of the halide ligand in (B) would give the metal a 16-electron configuration if the N 2 H 2 group remained a 2-electron donor. Instead it forms the isomeric di-anion of hydrazine, H 2 N-N 2  $^{\sim}$  and acts as a 4-electron donor. In both (A) and (B), the N 2 H 2 group is stable to further reduction. However, if the diphosphane is replaced by two mono-phosphanes, such as PMe 2 Ph or PMePh 2 , then such Mo or W dinitrogen complexes are reduced completely to

NH 3 plus some N 2 H 4 as in frans-[(N 2 ) 2 W(PMePh 2 ) 4 ] + H 2 S0 4 -> 1.9NH 3 + trace N 2 H 4 The Mo analogue yields 0.7NH 3 per mole of complex. The overall scheme postulated, via successive additions of H + , is M-N = N -> M-N = NH -> M = N-NH 2 -»• M-NHNH 2 -> M = NH + NH 3 : M = NH -+ M-NH 2 -> M(VI) + NH 3 The metal goes from (0) to (VI), and a number of the intermediates have been isolated. Experiments such as this have been carried out to clarify all the steps in the general scheme of Fig. 16.21, and several other minor paths have been found. The main thrust of the work, in addition to synthesis, has been the study of the protonation-deprotonation reactions of tnese nitrogen complexes leading to overall nitrogen fixation reactions such as L X M + N 2 -> L\*MN 2 + 6H+ -» L\*M + 2NH 3 There has also been considerable exploration of parallels between these nitrogen complexes and C 2 H 4 complexes or the various dioxygen species (compare previous section). The work on model fixation reactions may be summarized by saying that separate laboratory reactions are now known which reproduce many of the observed or postulated steps in the reaction of N 2 with nitrogenase, such as those in Fig. 16.21, but these have not been combined into one catalytic cycle. Different steps have been demonstrated with different nitrogen complexes, and S represents a variety of transition metal+ligand combinations, but not yet the natural substrate in nitrogenase. The whole fixation problem has turned out to be a very complex one. Three decades of work have led to an enormous increase in understanding and development of quite new classes of compound. 16.10.2 Bonding between N 2 and M Although many fewer N 2 complexes are found, their general properties are similar to the carbonyls (Section 16.1) and a similar linear bond is expected. This is indeed found in all structural studies of stable terminal nitrogen complexes (compare Fig. 14.29). The M-N-N M C=O an g | e is usua iiy very close to 180° and the NN bond, in accurately known structures, is in the range 112 + 2 pm, compared with 109.8 pm in the N 2 molecule. Again, as with Comparison of N 2 and CO carbonyls, the stretching frequency is found in the triple bond region, usually in the range bonded to a metal, M 1990-2160 cm" 1 compared with 2345 cm" 1 in N 2 . This all points to a bonding model for M-rfeN very similar to M-C=0 (see Fig. 16.2). However, there are significant differences. First (see Table 3.4), the highest filled orbital in N 2 is at -15.57 eV compared with -14.01 eV in CO. This is the a orbital involved in the a M <- NN (or M <- CO) bond. That is, the electrons donated to the metal are more tightly held in N 2 than in CO, and the a bond to the metal provides less energy in the nitrogen complexes. This is partly

compensated by the lower energy of the empty n\* orbital (-7 eV for N 2 , -6 eV for CO) involved in the n donation/ro/7? the metal M ->> NN or M ->> CO, but the difference of 0.6 eV (ca. 58 kj mol" 1 ) is an indication of the expected increased stability of the carbonyl over the dinitrogen system. This is reflected by the much smaller number of N 2 complexes known and by the fact that most contain only one N 2 group. In the M-N-N unit, the a donation is more important for the M-N bond formation than is the n back donation, and the end-on coordination should be appreciably stronger than the side-on configuration. The main effect of the n back donation in both configurations is to weaken the N-N bond, providing the required activation. In the side-on configuration, the N 2 unit

The carbonyl type of bridging is found when the

N-N bond order is reduced as in the imine

complex [Pt(PR 3 ) 2 N 2 H]2 +

bridges NH which contains the

The core of the tantalum complex containing an end-on,

side-on bonded N 2 ligand. Eac h Ta is also bonded to a

tridentate (PhNSiMe 2 CH 2 ) 2 PPh ligand (not shown). donates both G and n electrons to the metal, considerably weakening the N-N bond, and it is suggested that this may be the active intermediate in the reduction reaction. Although we have not discussed them in detail, the terminal metal acetylides, M-C=CH, are also very similar to the nitrogen complexes. When we come to bridging groups, we find a linear M-N=N-M system quite different from bridging carbonyls (compare Fig. 16.3b and d) but found for acetylides M-C=C-M. Here each M-N bond is similar to that in the terminal complexes, and a fully linear system is expected. As charge transfers are relatively small, and the total effect of the upper energy levels in M-N=N-M is approximately nonbonding for NN, we find the bond lengths and stretching frequencies in the bridged nitrogen complexes are generally similar to those in the terminal species, again comparable with the acetylides and in contrast to the bridging carbonyls. Although 'sideways-on' nitrogen, M— 1 1 1 , was postulated in reactions, stable complexes N with this bonding are rare. One report is of trans- (R 3 P) 2 Rh(Cl)N2 and the analogues X (R 3 P) 2 Rh(Cl)0 2 and (R 3 P)2RhCl(C 2 H 4 ) [R = CH(CH 3 ) 2 ]. Each contains a Rh- | unit (X = N, X O or CH 2 ) with the X
2 perpendicular to the RhClP 2 plane and its mid-point completing the square-planar configuration expected for Rh(I). The reaction with Rh is relatively weak. A new mode of N 2 binding has recently been determined in a complex containing two tantalum atoms; the N 2 unit is end-on bonded to one tantalum, and side-on bonded to the other tantalum. 16.11 Metal-dihydrogen complexes (a) o c c° c-" :M—co (b) c° M-co V.

FIG. 16.22 Complexes formed between a metal entity and H 2 :

(a) coordinated dihydrogen, (b) metal dihydride with M-H

bonds 16.11.1 Discovery In Section 15.5.1 we discuss the formation of the remarkable [ReH 9 ] 2 " complex which was unambiguously proved by X-ray and neutron diffraction (compare Section 7.4) to contain 9 M-H bonds. Following this and other determinations of complexes L X MH, it became accepted that H could act as a ligand even in complexes of metals in states which are relatively strongly oxidizing. Polyhydrides of the more stable high oxidation states such as Ta(V), W(VI) or Os(VI) are noted in Chapter 15. It was also widely accepted that metaldihydrogen units, M-H 2 , were intermediates in the activation of H 2 by metal catalysts, and low-temperature matrix studies gave evidence for species such as Pd(H 2 ) and Cr(CO) 5 (H 2 ). In 1983 startling evidence appeared that the H 2 molecule could coordinate as an entity in complexes which were stable at room temperature. During a study of S0 2 complexes a purple compound turned yellow under N 2 and yielded the dinitrogen complex M(CO) 3 L 2 (N 2 ), from which the N 2 could be displaced to form the desired SO 2 complex. The purple compound was later identified as the 16-electron intermediate M(CO) 3 L 2 (M = Mo, W; L=a bulky phosphane such as P(zso-Pr) 3 ). The significant discovery was that H 2 behaved in exactly the same way as N 2 to give a yellow complex containing 2 H on addition to the purple intermediate. Furthermore, addition of N 2 resulted in replacement of H 2 by nitrogen to give the dinitrogen complex. Two interpretations were possible: (i) that two normal M-H bonds were formed giving M(CO) 3 L 2 (H) 2 (Fig. 16.22b) and involving oxidation to M(II) which happens to be yellow, or (ii) that a new type of molecule is formed, M(CO) 3 L 2 (H 2 ) (Fig. 16.22a), in which dihydrogen is bound as a molecule as N 2 is in dinitrogen complexes. The experimental resolution of this question is interesting as it highlights the need that often arises to use a combination of techniques. First, the infrared spectrum showed no band in the regions 2300-1700 cm" 1 and 900-700 cm" 1 where M-H stretching or bending occur, but

there were bands at 1570, 960 and 465 cm" 1 which shifted in the D 2 analogue, as expected from the mass effect (see Section 7.7) for vibrations involving hydrogen. An X-ray crystal structure study can often not detect H in presence of heavy

420

See Section 9.7 for a discussion of hydrogen

hydrogen bonding involving metal-hydride

compounds

FIG. 16.2 3 a donation and n back-donation proposed for the

M-H 2 interaction atoms, and there were additional experimental problems involving disorder. The incomplete structure that emerged did show the three CO and the two phosphane ligands in octahedral positions, suggesting that the hydrogen occupied the sixth site. The hydrogen was located using neutron diffraction on the W complex, which showed an H-H unit coordinated sideways on to the metal, parallel to the P-W-P axis (Fig.16.22a). However, the disorder left some remaining doubt and since this totally new mode of bonding by H 2 required further proof, nmr studies were undertaken. Metal hydrides have a characteristic resonance position and the H signal is split by coupling to the P atoms and to the magnetic 183 W isotope (Section 7.8). Any coupling between two M-H bonds would be fairly small and give a doublet. For W complexes sharp lines would be expected. The yellow hydrogen complex showed a resonance close to the M-H range but the signal was unexpectedly broad. The HD analogue was therefore made for nmr study. D has a spin 1=1 and therefore gives a 1:1:1 triplet on coupling. This was indeed found with /(H-D) = 33.5 Hz whereas for coupling between separate M-H and M-D bonds, / is 1-2 Hz. In addition, the HD complex now showed a band in the infrared at 2360 cm" 1 , which was assigned as the HD stretch (the H-H stretch was later detected in the region 2700-3000 cm<sup>"</sup> 1 in M(H 2 ) complexes). This adds up to strong supporting evidence for the complex and also shows that the W-H 2 structure persists in solution. Additional nmr effects, especially the. relaxation times, were also found to be characteristic of dihydrogen coordination. Other dihydrogen complexes were quickly identified including hydrogen-dihydrogen species such as [MH(H 2 )L 4 ] + (for M = Fe, Ru, Os) and even [IrH 2 (H 2) 2L2] + . In most examples L x = phosphane or a combination of phosphane with ligands like CO or cp. The

series M(CO) 3 L 2 (H) 2 was completed by the synthesis of the M = Cr species, which was stable only under an atmosphere of H 2 . Re-examination of some of the established polyhydrides led to their re-formulation as dihydrogen complexes. Nmr and neutron diffraction established the structure MH 2 (H 2 ) (PR 3 ) 3 (M = Fe, Ru) a much more comfortable status than the original formulation as a 7-coordinate Fe(IV) tetrahydride. However, many polyhydrides remain established as solely M-H compounds. While there was some question about Re (VII) species, the current conclusion is that the ReH 7 L 2 analogues of [ReH 9 ] 2 ~ are indeed Re(VII) heptahydrides and not dihydrogen complexes of Re(V). 16.11.2 Properties and bonding The H-H bond distance is best determined by neutron diffraction or nmr methods. The observed values range from 85 pm to 102 pm (compare H 2 = 74 pm, Chapter 9). The values of the HD coupling in the nmr vary from 35 to 22 Hz, and the coupling decreases as the bonds get longer—as expected, since the coupling is mediated by the bonded electrons (/(HD) =43.2 Hz for the free molecule). The H-H stretching frequency ranges from 3080 to 2690 cm" 1 , with the corresponding H-D values around 2300 cm<sup>"</sup> 1 (compare free H 2 at 4390 cm" 1 and HD at 3820 cm" 1 ). The other infrared bands are the M(H) 2 stretches in the 1500 cm" 1 and 900 cm" 1 regions and lower frequency bending modes. The heat of formation of the dihydrogen W complex from the purple intermediate is measured as -42 kj mol" 1 compared with -57 kj mol" 1 for the corresponding N 2 compound. All these properties indicate an interaction which weakens the H-H bond compared with the H 2 molecule. As H 2 is extremely simple, with no accessible orbitals other than a and cr\* (Fig. 3.6b), the interaction with the metal must involve only these. The proposed model is shown in Fig. 16.23 and involves a side-on orientation with donation from the H 2 a bonding orbital into an empty metal d orbital, supported by back-donation from a filled metal orbital into a\*. The model is closely analogous to the long-standing one for ethylene-M coordination (Fig. 16.6b), except that there the TL orbitals were involved. The effect of such an electron transfer is to weaken the H-H interaction, especially by back-donation, in order to gain the M-H interaction. The system is very delicately balanced but, as the H-H bond is very strong, some weakening is tolerable before dissociation occurs. The back-donation is thought to be important for the formation of M(H 2 ) complexes since acceptors which lack filled d orbitals do not form them. More detailed calculations show that the o interaction is CHAPTER 16 the major one, and give values for the parameters which are a good match to the observed ones. For many complexes there is nmr evidence

in solution for dissociation of the dihydrogen complex into 2MH bonds, i.e. an equilibrium between forms corresponding to Fig. 16.22a and b. The dihydrogen complexes thus capture the initial stage of hydrogen activation and support the model proposed for the mechanism of metal catalysis. It is reasonable to apply a similar model to other cases of activation of strong single bonds, such as C-H. It has been observed that C-H bonds in ligands such as phosphanes sometimes lie in an abnormal position close to the transition metal in what is termed an agostic interaction, suggesting bond formation of a type very similar to that proposed for dihydrogen. One example is found in the 16-electron purple intermediate above. This clearly models the first stage of C-H activation. Similar activation is seen in Wilkinson's compound, RhCl(PPh 3 ) 3 , where an H of one of the phenyl groups of the phosphane ligand coordinates agostically to Rh, explaining the good hydrogénation catalyst properties of the complex. 16.12 Post-actinide 'superheavy 7 elements 16.12.1 Background For the elements up to about Z= 100, the mode of decay is principally by a- or jS-particle emission and it is the likelihood of these events which governs the half-lives. It will be seen from Table 12.1 that the half-lives tend to decrease as Z increases. However, at about the atomic number of the heaviest elements, another mode of decomposition, spontaneous fission, becomes the dominant one. In this mode half-lives again decrease with increasing atomic number. Estimates of isotope stability require an understanding of the binding forces in the nucleus, and this has only slowly developed. Earlier approaches were too pessimistic and the experimenters continued to find isotopes which were longer lived than expected. For example, initial estimates suggested that the half-life for spontaneous fission decay would be a few seconds for element 103 and would have dropped to about 10~ 4 seconds by element 110, making it unlikely that elements in this range could be synthesized. A decade or so later, several isotopes of lawrencium, Z= 103, had been reported and the longest half-life, Lr-262 = 214 minutes, was about 500 times longer than predicted. While this suggested that it would be somewhat easier to reach heavier elements, the expectation remained of ever-decreasing half-lives as Z increased. At the same time, the experimental difficulties of synthesizing new nuclei remained enormous and required skilled and very specialized teams. Much of the work for several decades was done by groups of experimenters in the United States and in Russia, and these were joined more recently by a team in Germany. (See the box titled The race to superheavy elements'.) In the last decade or so, the pace of new discoveries has picked up, with element 112

indicated in 1995 and 114 plus new isotopes of earlier elements by 1999. In this atomic number zone, a new feature of nuclear structure comes into play. Theorists predict an 'island of stability' based on 'magic numbers' of protons for 7= 114, 120 or 126. These magic numbers reflect the existence of 'closed shells' of protons and neutrons in the nucleus (broadly analogous to the stable electron shells of the rare gas configurations), which provide a further barrier to decay, offsetting the overall decline in stability with increasing Z. While the latest discoveries are still too neutron-poor to reach the point of highest predicted stability, they do show much longer half-lives than would be extrapolated from elements 104 to 110. 16.12.2 Synthesis and properties The actinide series is complete at lawrencium, Z= 103 (see Section 12.7). The same techniques of bombarding actinides with accelerated nuclei of light atoms produced the next two elements, 104 and 105. Thus, bombarding californium with 15 N nuclei gave an isotope of 105, Unp-260, which has a half-life of 1.6 s and decays to Lr-256 with emission of an a-particle. The routes to the heavier elements have used preferred targets whose nuclei are close to the 'magic numbers', corresponding to high stability. Thus elements 106 to 109 have been approached through lead or bismuth targets corresponding to 7=82 or N= 126, and the energy of the bombarding particle is kept relatively low in the 'cold fusion' approach. Thus an announcement of the synthesis of element 109 from Darmstadt involved bombarding Bi-209 with accelerated Fe-58 nuclei. Only one in 10 14 interactions gave element 109, which was formed at the rate of one atom in a week. Identification was purely by use of nuclear properties (using a new velocity filter technique for separation), and four independent properties matched calculation. Decay was by successive oc-emissions to Bh262, then to Db-258 and then by electron capture to Rf-258. Similar experiments yielded a few atoms of element 111 and 112 in the period 1994-6. Overall, the Darmstadt methodology allowed a significant jump forward, yielding elements 107 to 112. This approach has two advantages: (1) the a-decays are well defined and eventually lead to a known daughter product, allowing identification through the chain; (2) as the initial products contain more neutrons than protons and the a loss removes two of each, the daughter products may be more neutron-rich and of longer half-lives than the isotopes of such daughter elements which were directly synthesized. This latter effect is one reason why an initial discovery of an element is often followed by the report of further isotopes with longer half-lives. Despite these advantages, the Darmstadt technique was reaching its limits and much higher accelerating energies would be

needed to go to Z values above 112. In a further leapfrog the USA team at Berkeley and the Russian group at Dubna have each achieved elements above 112. The Berkeley experiments used the same approach as the German one but followed a prediction that a particular magic number pair—Kr-86 plus Pb-208—would produce element 118. A positive claim was made in 1999 that three atoms were seen of the 293 isotope of element 118 which decayed by a series of a emissions through Z= 116, 114, 112, 110, 108 to lOoSg. Unfortunately, the work could not be repeated and the claim was withdrawn in 2001. This incident underlines the extreme difficulty of such experiments, but also gives confidence in the checking procedures in place. Also in 1999, the Dubna team reported experiments using much higher bombarding energies to react the rare, but very neutron-rich, isotope 48 Ca with targets of U or Pu. The high energy increases the probability of fusing the two nuclei, but also increases the probability of fission, and gives a messier system. Bombarding 238 U gave two events assigned to the isotope of element 112 with mass of 283 with a half-life of 1.5 minutes (much longer than the 277 isotope prepared earlier). Similar experiments using Pu-244 gave a single atom of element 114 of mass 289 which decayed by three oc emissions through elements 112, 110 to 108 which then fissioned. A third experiment showed that starting from the lighter Pu isotope of mass 242 gave the isotope of element 114 of mass 287. This decayed to the same isotope 283 112 which was made from uranium-238, as expected. These three experiments were self-consistent. While the product mixes from the Dubna method were more difficult to analyse, it complements the Berkeley approach in giving more neutron-rich isotopes, which have longer half-lives. It highlights the difficulties, and also the immense sophistication of the experimental techniques, to note that in all these experiments only about one in a trillion of the bombarding atoms produces one of the new nuclei. Table 16.7 summarizes the properties of the post-actinide elements reported by 2001. For element 104, rutherfordium, tracer studies show properties expected for the 6d congener of hafnium. Thus it forms RfCl 4 , comparable to HfCl 4 and unlike the involatile trichlorides of the actinides and lanthanides. Rutherfordium was manipulated in solution as the hydroxybutyrate anión and its tracer behaviour followed hafnium. Thus rutherfordium behaves as the first post-actinide element, as the heaviest element of the titanium Group. Dubnium, element 105, formed a chloride and a bromide, which were more volatile than the hafnium tetrahalide but less volatile than the niobium pentahalides. DbBr 5 has an estimated boiling point of

430°C. Tracer experiments showed that dubnium adsorbs to glass like niobium and tantalum, but in contrast to zirconium and hafnium. Thus dubnium is assigned as the heaviest element of the vanadium Group. However, in solvent extraction experiments, dubnium remained with niobium in the aqueous phase while tantalum extracted into the organic phase, showing that properties of the heaviest element cannot always be predicted by simple extrapolation from the 4d and 5d congeners. The chemistry of seaborgium, element 106, has also been studied thanks to the relatively long half-lives of the 265 and 266 isotopes. In several tracer experiments, Sg followed Mo and W(VI) and did not follow U(VI). The species formed were probably oxy- or oxyhalide complexes such as [Sg0 4 ] 2 ~, Sg0 2 F 2 or [Sg0 2 F 3 ]~. Seaborgium therefore fits as the 6d series member of the chromium Group. For bohrium, the preparation of the longer-lived Bh-267 isotope allowed the identification of the very volatile Bh0 3 Cl behaving as the heavier homologue of Tc and Re. Similarly, hassium behaves as a reasonable extrapolation from Ru and Os. To date, there has been insufficient material to study the heavier elements from meitnerium onwards. Theoretical calculations of properties such as gas chromatographic or

## THE RACE TO SUPËRHEAVY ELEMENTS

Because of the experimental difficulties, there have been conflicting claims to be the first to synthesize several of the new 'superheavy' elements (including the later actinides). The Russian team used heavy ion bombardment which allowed leaps forward in Z but gave isotopes which decayed by spontaneous fission. These were more difficult to identify unequivocally than the American experiments which used only stepwise advances in Z. This approach had the advantage that it gave isotopes decaying by alpha particle emission into directly identifiable daughter products. Cold War suspicions precluded any colla boration in a field as sensitive as nuclear chemistry. The result was that competing claims arose between the Russians and the Americans for priority in discovery and for the right to propose names for the new elements. As a result, different names for particular elements got into the literature. By international agreement, the final decision on names is made by the International Union of Pure and Applied Chemistry, IUPAC. It was agreed that a new element would be accepted only after it was produced by two independent experiments. Often, a long time was required to sort out competing claims and provide the verifying observations. Some of this confirmation came from the German team with a new methodology. A systematic terminology was proposed by IUPAC for use until formal names were finally decided. The ten numbers are shown by 0 nil 1 un 2 bi 3 tri 4 quad 5 pent 6 hex 7 sept 8 oct 9 en Names are formed from these number elements in order with rules about elision. For example, element 104 is named unnilquadium and the symbol is Unq. While this scheme gives rather unlovely names, it is

unfortunate that it was not generally adopted, as much confusion would have been saved. An interim determination of names was published by IUPAC about 1995, but this led to further heavy lobbying and a number of changes were made in the final determination of the official names. In this edition, the official names are used throughout—for example, in Tables 2.5 and 16.7, and elsewhere in this section. However, as many of the alternative names for the superheavy elements have had some currency in the literature, these are recorded for reference below Element 104 105 106 107 108 109 Proposed names Dubnium Rutherfordium Kurchatovium Unnilquadium Joliotium Neilsbohrium Hahnium Unnilpentium Rutherfordium Seaborgium Unnilhexium Bohrium Neilsbohrium Unnilseptium Hahnium Hassium Unniloctium Meitnerium Unnilennium Proposed symbol Db Rf Ku Ung Jl Ha Unp Rf Sg Unh Bh Ns Uns Hn Hs Uno Mt Une Proposer Interim IUPAC USA Russia IUPAC systematic Interim IUPAC Russia USA IUPAC systematic Interim IUPAC USA IUPAC systematic Interim IUPAC Germany IUPAC systematic Interim IUPAC Germany IUPAC systematic Interim IUPAC, Germany IUPAC systematic

TABLE 16.7 Superheavy element isotopes Element 104 rutherfordium, Rf 105 dubnium, Db 106 seaborgium, Sg 107 bohrium, Bh 108 hassium, Hs 109 meitnerium, Mt 110 111 112 114 Isotope 257 259 261 258 262 263 265 266 261 264 267 265 267 266 268 269 271 272 277 283 287 289 Half-life 0.8s 1.7s 65 s 4 s 34s 27s 7 s 21 s 12 ms 0.45 s ca. 20 s 1.8 ms 74 ms 3.4 ms 72 ms 0.17 ms 1.1 ms 1.5 ms 0.28 ms 1.5 min 5.5 s 34 min? Other isotopes All from 253 to 255, 257, 260, 259, 260, 261, 262 264, 269, 277 267, 273, 281 271 285 262 261 263 Predicted centre of island of stability: 7= 114, mass = 298. solution chemistry match reasonably with observations for the earlier elements and thus give a reasonable indication of the probable behaviour of the heavier ones. All this work was carried out on a tiny scale, often using only a few tens of atoms. Earlier experience with the post-uranium elements was that interpretations based on tracer studies were often amended when larger quantities became available. With such reservations in mind, the observations to date are in accord with the view that the superheavy elements from rutherfordium onwards are filling the 6d post-actinide period. If this is the case, meitnerium, 110, 111 and 112 complete the 6d series. The next elements are expected to be members of the Main Groups, with the outermost electrons in the 7p shell. If it is possible to reach element 123, we may find that the first g level, the 5g shell, will start to fill. A little further on, theZ= 126 magic number presents a variety of interesting possibilities, as we would expect the 5g, 6f and 7d levels to be very close in energy. Recently discovered element 114 is expected to be 'ekalead' while 118 would be the heaviest member of the rare gas Group. If the half-lives in this area of the Periodic Table are as

long as predicted, and if the developing new methods give sufficient yields, then there are exciting possibilities for a relatively well-developed chemistry. Already predictions are being made—for example, that 114 will be even more stable than lead in the +11 state and that 115 will have a stable +1 ion. Perhaps the next edition will see a more extended discussion—transferred to its correct position in a Main Group chapter! The estimated 'centre of the island of stability' comes at even higher neutron numbers around a mass of 298 for element 114. Thus these latest experiments arouse great interest, as the higher Z values and the lengthening half-lives seem to show we are approaching the stable region. New or improved methods are also being developed. 16.13 Relativistic effects When the nuclear charge becomes large, the radial velocity of the inner electrons rises to become a significant fraction of the speed of light. This can be envisaged on a simple planetary model—as the positive charge on the nucleus rises, the negative electron has to move faster to remain in a particular orbit. Calculations show that, for elements around Hg withZ= 80, the average radial velocity of the Is electron is about 60% of the speed of light. At such speeds, the special theory of relativity shows that the mass increases, by about 20%, and, as a result, the average radius of the orbital contracts by about 20%. The effect is most prominent for orbitals with electron density close to the nucleus, so the main effect is on s orbitals. There is a lesser effect on p orbitals with m∖ = 0 but not on the +1 or -1 values, causing a splitting of the p set into groups of 1 and 2 orbitals. There are two principal consequences. First, the s orbitals of the heavier elements become more stable than otherwise expected, and therefore have higher ionization potentials for electron loss or more exothermic electron affinities for electron gain. The second consequence is that the more contracted s orbitals shield the outer orbitals of the d and f sets more effectively from the nuclear charge, so that these orbitals expand and their energies are less. The chemical consequences are seen mainly in the heaviest elements. While the lanthanide contraction accounts for the similarity between the 4d and 5d series, it has been calculated that relativistic effects contribute about 20% to the contraction of Hf, so that the extremely close similarity between the earlier members of the two series depends in part on the relativistic effect. As we move along the 5d series, the resemblance to the 4d congener decreases (compare Sections 15.6 to 15.10) and this is a combination of both relativistic effects. The reduced binding of the 5d electrons allows them to participate more fully, which is seen in the increasing number and stability of the higher oxidation states.

Examples are Pt(IV) or Au (III) versus the much less stable Pd(IV) or Ag(III), and the existence of Pt(VI) or Au(V) with no Pd or Ag counterparts. Other examples are clear in Chapter 15. A second effect is the stabilization of the 6s 2 configuration. This can be clearly seen on comparing the properties of mercury with its neighbour, gold (and also to a lesser extent with thallium). Metallic mercury has anomalously low melting and boiling points, is monoatomic in the gas phase and the density of mercury (13.53 g cm~ 3 ) is markedly different from that of gold (19.32 g cm" 3 ). Mercury thus appears to be behaving as if it has a rare-gas electronic configuration and this can be nicely accounted for by the stabilization of the 6s 2 configuration by relativistic effects. A similar effect, which has been encountered previously (Section 15.9.2), is the striking tendency of gold to adopt the same 6s 2 configuration in the Au~ ion. Thus, the intermetallic

GOLP IS SMALLER THAN SILVER

Gold is often described as having a covalent radius Me which is the same, or slightly larger, than that of its lighter Group member, silver. However, as a result of a relativistic contraction, described in this section, it has been predicted that gold should be slightly smaller than silver. Until 1996, no experiment had been carried out which could give unambiguous results. The experiment involved synthesizing analo gous complexes of gold(I) and silver(I), with the same ™ei.o«t^^ ligands and counteranions, the same coordination geometry, isomorphous crystal structures, and equal experimental conditions. Bis(trimesitylphosphane) (=L) complexes were prepared as their BF^r salts, 133pm respectively, which corresponds to a reduc i.e. [L 2 M] + BFi~, and characterized by X-ray diffraction. tion in covalent radius of 6% on going from

The two complexes had identical structures, except gold,

that the Au-P bond length was 0.09(1)A (9pm)

smaller for gold than for silver. The covalent radii of Reference

gold(I) and silver(I) were thus calculated to be 125 and /. Amer. Chem. Soc. 118, 1996, 7006-7007. compound CsAu is a semiconductor rather than a metal and has a significant amount of ionic character, Cs + Au~. Consistent with this, gold has the highest electron affinity and electronegativity outside of the 'typical' electronegative elements, higher than sulfur and almost as high as iodine. Again, gold is showing a strong tendency to form a stable 6s 2 configuration. In addition, the surprisingly stable gas-phase Au 2 molecule has a stronger bond dissociation energy than I 2 (221 vs 151 kj mol" 1 ), and gold, in many respects, can be thought of as a pseudo-halide analogous to iodine, both elements being one electron short of an inert-gas electronic configuration. Another phenomenon in gold chemistry arising from relativistic effects is the strong tendency for gold to form Au- • -Au contacts in the solid state, similar to halogen- • -halogen interactions in organic compounds. The energy of this interaction has been estimated to be as strong as 30 kj mol" 1 , comparable with a hydrogen bond, and this is therefore a significant factor in determining the solid-state structures of gold complexes. A further manifestation of relativistic effects in chemistry is the Inert pair' effect in the heaviest Main Group elements Tl, Pb and Bi, where the most stable oxidation state is two less than the Group oxidation state (compare Sections 17.1, 17.3 and the chemistries of these elements). This is again nicely accounted for by the relativistic stabilization of the 6s 2 configuration. The relativistic contraction does not change smoothly with Z, but increases markedly while the 5d shell is filling, with the maximum effect at Au. The effect diminishes to Bi and then changes only slowly through the 5f shell so that effects comparable to Au are seen only around Fm. It appears that the chemistry of the superheavy elements will eventually develop, though probably rather slowly, and the influence of relativistic effects on the chemistry of these elements should prove very interesting indeed. Recent relativistic calculations on the superheavy elements has suggested that these effects may be quite subtle, particularly with regard to p orbital occupation. One interesting pointer is the possible configuration of Lr

where the last electron may be in the 7p level rather than the 6d one, as a consequence of the relativistic effect on the m = 0 level. It has also been recently suggested that the ground state electronic configuration for element 104 (rutherfordium) may be [Rn] 5f 14 od 1 7s 2 7p !, while on the other hand that of element 105 (hahnium) may be [Rn] 5f 14 od 3 7s 2 , by analogy with the configuration of tantalum. Around ekalead (element 114) there exists the possibility of an Inert quartet' effect. The relativistic effect is not the only contribution to the unusual chemistry of the heavier elements, and other rationalizations of the inert pair effect have been proposed, but it is a substantial contribution. It is clear that calculated changes in the relative energies of the s and d levels are in accord with observation and account for many of the unusual features.

## Problems

16.1 Discuss the following organometallic compounds in terms of the 18-electronrule: (i/ 6 -C 6 H 6 )Cr(CO) 3 (;? 5 -C 5 H 5 )Ni(NO) Mn 2 (CO) 10 Fe 3 (CO) 12 (/7 5 -C 5 H 5 )Fe(CO) 2 Br ' Mn(CO)+

16.2 Why is the average C-0 stretching frequency in the infrared spectrum of (Ph 3 P) 3 Cr(CO) 3 lower in energy than that of Cr(CO) 6 ? Compound v(co) 6 Mn(CO)+ C-0 stretching frequency (cm1 ) 1860 2090 M-C stretching frequency (cm1 ) 460 416 16.3 Explain the following infrared spectroscopic data:

## 17 CHAPTER 17 THE ELEMENTS OF THE 'P' BLOCK

Proposed structure of B 8 F 12 Although A1 2 O and A10 have been identified in the vapour phase above 1000°C, aluminium chemistry at ordinary temperatures is almost entirely of the III state. The formal II state, arising from an A1-A1 bond is found in species formed by R 2 A1X + 2K -> R 2 A1-A1R 2 + 2KX where R is a bulky organic group like (CH 3 ) 2 CH. With smaller R groups, or on heating, R 3 A1 and aluminium metal are formed. A1C1 2 has also been reported. Boron is found in low formal oxidation states in the hydrides and in a variety of halides. The latter include the dihalides, B 2 X 4 , and lower-valent boron fluorides which are related to BF 3 by replacing F by a BF 2 group: (F 2 B) n BF 3 . n for n = 0,1,2 and 3. These are prepared by treating B 2 C1 4 with SbF 3 or by strongly heating BF 3 with boron. FB(BF 2 ) 2 disproportionates at -30°C, to give BF 3 and B 8 F 12 , while the n = 3 member is not stable alone but does form adducts with L - CO or PF 3 , (BF 2) 3 BL analogous to H 3 BCO or H 3 BPF 3. It has been suggested that the rather unstable B 8 F 12 is an analogue of diborane. Like diborane, it gives monomer adducts B 8 Fi 2 + CO -> (BF 2 ) 3 BCO (compare B 2 H 6 + CO -» H 3 BCO). 17.5 The carbon Group, r?s 2 A?p 2 17.5.1 General properties of the elements, uses Table 17.8 summarizes some properties of the elements, and the variation with Group position of ionization potentials, radii and oxidation state free energy is indicated in Figs 17.17 and 17.18 Carbon reacts, when heated, with many elements to give binary carbides. Numerous suicides also exist and these are similar to the borides in forming chains, rings, sheets, and three-dimensional structures. Table 17.9 summarizes the various carbide types and Figs 17.19 and 5.13 give some of the structures. The carbon Group shows the same trend down the Group towards metallic properties as in the boron Group. The II state becomes more stable and the IV state less stable from

TABLE 17. 8 Properties of the elements of the carbon Group Element Carbon Silicon Germanium Tin Lead Symbol C Si Ge Sn Pb Structures of elements G , D D D D, M M Oxidation states IV IV (II), IV II, IV n, (iv) Coordination numbers 4 , 3 , 2 4, (6) 4 ,6 4 ,6 4, 6 Availability Common Common Rare Common Common G — graphite, D — diamond and M = metallic forms

elements include: Ionization potentials Atomic properties and electron configuration Radii Electronegativities Redox potentials Hydrides Structures of elements Structures of silicates Table 2.8 Table 2.5 Table 2.10 Table 2.14 Table 6.3 Chapter 9 Sections 5.9, 19.3 Section 18.6 The use of carbon in metal extraction is discussed in Section 8.7. Fullerenes and related forms of carbon are covered in Section 19.3, silicates in Section 18.6 and cluster ions of the heavier elements in Sections 18.4.4 and 18.4.5. See also Section 20.1.3 for the role of silicon in biochemistry and Section 20.3 for the environmental impact of these elements, especially the role of carbon compounds in the ozone hole and the greenhouse effect.

OCCURRENCE AND USES OF THE CARBON GROUP ELEMENTS All the elements are common except germanium, which occurs as a minor component in some ores, and also in trace amounts in some coals. Carbon, of course, occurs in all living things, and in deposits derived from them such as coals, oils and tars. Hard coals like anthracite have high carbon contents. Heating coals to form coke removes hydrogen components, leaving carbon con taining a low percentage of metal compounds. Pure carbon is formed by pyrolysis of hydrocarbons and, as graphite, finds substantial industrial and electrical uses. While production of artificial diamonds is feasible, large pressures and temperatures are needed. More recently diamond films have been produced on metals by deposition from vapour-phase decomposi tion of methane, by plasma methods or by ion-beam deposition. Such interest in diamonds stems from their optical and semiconductor properties, and the ability to deposit films would be of great advantage where wear resistance is required. Silicon, with oxygen, is the

## major component of the

Earth's crust and the vast majority of rocks, minerals and their breakdown products the sands and clays, are silicates. Tin occurs in concentrated deposits as the oxide cassiterite, SnO 2 . Lead also occurs in concen trated form as the sulfide, galena, PbS. As both Sn and Pb are readily formed from their ores by heating with carbon in the form of wood fires, these two metals were among the earliest to be produced and used by humans. Lead was particularly widely used by the Romans for water pipes ('plumbing' comes from Latin Plumbum, lead) while tin was the vital additive to copper (also an ancient metal) to form the much harder alloy, bronze. Current uses still reflect the ancient patterns, with much of tin consumption being in alloys, and lead being phased out from water supply uses only in the second half of the 20th century as awareness of its toxicity increased. About half of modern tin production is used in tin plate, where its inertness protects the underlying steel. Another use is in glass manufacture where the absolutely smooth surface required for the formation of sheet glass is provided by a bath of molten tin (making use of the inertness and nontoxicity of tin). A major outlet for both metals is in alloys—so/ders which are basically Sn/Pb, type metals which are Sn/Pb/Sb,

pewters which are now mainly Sn/Sb but formerly contained some Pb, bearing alloys which are around 9 Sn to 1 Pb, and the tin-copper alloys bronze and brass (with Zn). All such alloys have a range of compositions optimized to different uses, and contain a number of other elements as minor components to refine the

properties. The toxicity of lead is starting to limit some of its traditional uses, such as ceramic glazes. (It is thought that some of the less rational behaviour of the Roman emperors was due to lead poisoning from glazes used on wine jars.) It is widely used in batteries, in priming pigments, in sheathing for heavy-duty cables, as well as in alloys. The structures of the elements are discussed in Section 5.8 and illustrated in Fig. 5.14. First germanium, and then silicon, became extensively used in very pure forms in semiconductor devices, which are at the basis of the whole electronic industry, including computer hardware. Germanium now accounts for only a few percent of the electronic uses, and other materials, like the binary GaAs, make significant contributions, but the major use is of silicon. Since the detailed tailoring of a semiconductor demands the controlled addition of different elements at less than the parts per million level, silicon or germanium are first produced from purified oxide, via a cycle of MC1 4 distillation, and reduction to the element. They are then produced in very high degrees of purity (better than 1:10 9 ) by zone refining. In this process, the element is formed into a rod which is heated near one end to produce a narrow molten zone. The heater is then moved slowly along the rod so that the molten zone travels from one end to the other. Impurities are more soluble in the molten metal than in the solid and thus concentrate in the liquid zone which carries them to the end of the rod. Uses of compounds of the carbon Group elements include all the well-known industrial organic chemicals like the oil and plastics industries (see below for uses of organometallic compounds of the other elements of the Group). Silicon dioxide and silicates are the major components of glasses, ceramics, pottery and related products, while pure SiO 2 is important in finely divided high surface area forms for adsorption uses in industry, medicine and the laboratory. Fused silica is a very high melting, inert, glass with very low expansion coefficient. Silicon carbide, SiC, is the abrasive carborundum. Tin dioxide is a component of

heterogeneous catalysts, is used widely in ceramics and enamels, and—as a very thin film—in electroluminescent devices. Treatment of glass with SnCl 4 deposits a thin film of SnO 2 on the surface which adds markedly to the toughness. All the carbon Group elements are fairly unreactive, with reactivity greatest for tin and lead. They are attacked by halogens, alkalis and acids. Silicon is attacked only by hydrofluoric acid, germanium by sulfuric and nitric acids, and tin and lead by a number of both oxidizing and non oxidizing acids. carbon to lead. Carbon is a nonmetal and occurs in the tetravalent state. Silicon is metalloidal, but nearer nonmetal than metal, and forms compounds only in the IV state, apart from the occurrence of catenation. Germanium is a metalloid with a definite, though readily oxidizable, II state. Tin is a metal and its II and IV states are both reasonably stable and interconverted by moderately active reagents. The Sn 4+ /Sn 2+ potential is -0.15 V and 447 Si Ge Sn Pb FIG. 17.17 Some properties of the carbon Group elements/This figure shows the variation, with Group position, of the atomic radii and the sum of the first four ionization potentials. The characteristic differences between first and second elements, and the similarity between second and third elements, are noticeable here tin(II) in acid is well known as a mild reducing agent. Lead is a metal with a stable II state. Lead (IV) is unstable and strongly oxidizing. The elements of the carbon Group are particularly characterized by their tendency to catenation, i.e. to form chains with links between like atoms. Carbon, of course, has this property in an exceptional degree. In the hydrides, chains of up to ten atoms are established for silicon and germanium, as in Sii 0 H 2 2, and distannane, Sn 2 H 6 is known. Silicon also forms long-chain halides but germanium is limited to GeCl 4 and Ge 2 Cl 6 as far as present studies go. However, when the chain is fully substituted by organic groups, as in M n (CR 3 ) 2 n+2, there is no apparent limit to /? for M = Si, Ge and Sn. In these compounds, as with silanes and germanes, the restriction is the experimental difficulty of handling high molecular-weight compounds. While the hydrides readily oxidize, and the halides xPb Si oxidation state IV FIG. 17.18 The oxidation state free energy diagram for elements of the carbon Group. It will be seen that Ge(ll) is unstable, Sn(ll) of nearly the same stability as Sn(IV), and Pb(IV) is very unstable relative to Pb(ll) I 11 3 J2 o « ï| ^ s •5 a E (0 <^» 3 1 \_u i ï u §• <

TABLE 17.9 Types of binary carbide O Th O-O C 2

FIG. 17.19 Structure of thorium carbide, ThC 2 . As in CaC2,

the C 2 units occupy halide ion positions in a NaCI-type

structure but differ in being oppositely aligned in successive

layers (compare Fig. 5.13) hydrolyse rapidly in air, the organo-derivatives are moderately stable to attack by air. Lead compounds are more restricted, but Pb 2 R 0 species are well known. In addition, these elements form compounds (MR 2 ) n which are ring compounds. Rings with n = 4, 5 and 6 are well known for M = Si, Ge and Sn, for R = Ph or related aryls, and some alkyl species are reported as well. For example, Me 10 Si 5 has been made and converted to Me 9 Si 5 X (X = Cl, Br) which allows further reaction. A few three-membered rings occur but only with bulky ligands. Larger rings are established for Si and Sn. There is also definite evidence for the formation of branched chains. The compounds (Ph 3 Ge) 3 GeH and a number of mixed silylgermanes, (H 3 Si) n GeH 4 \_ n (n = 2, 3, 4), and methyl derivatives, (H 3 SiyCH 3 )GeH 3 \_ n (n = lj 2, 3), have been reported. Branched chain hydrides of M 4 and M 5 forms (M = Si, Ge) are also indicated by chromatographic experiments. For tetrasilanes and tetragermanes, the n- and iso- forms have been separated on the macroscale, as have two of the three Ge 5 H 12 isomers and related silicon-germanium species (see Section 9.5). Recently, a number of compounds (Ph 3 M) 4 M / (M = Ge, Sn, Pb and M' = Sn, Pb) have been reported. The pentaplumbane of this fleo-form, Pb(PbPh 3 ) 4 , is the only other species with Pb-Pb bonds.

State of aggregation

of the carbon atoms

Single atoms

- (a) Salt-like carbides
- (b) Transition element

carbides

Linked carbon atoms

(a) C 2 units 'acetylides'

(b) C 3 chains

Carbon sheets (lamellar structures

(a) Buckled sheets

(b) Planar sheets Properties Yield mainly CH 4 on hydrolysis (i) Conducting, hard, high melting, chemically inert (ii) Conducting, hard, high melting, but chemically active: give C, H 2 , and mixed hydrocarbons on hydrolysis (i) CaC 2 type — ionic, give only acetylene on hydrolysis (ii) ThC 2 type — apparently ionic, give a mixture of hydrocarbons on hydrolysis Gives propyne, H 3 C-C=sCH, on hydrolysis C-C spacing in chain is similar to that in hydrocarbons derived from graphite) Nonconducting, carbon atoms are 4-coordinated Conducting n system is preserved Examples and structures Be 2 C (antifluorite) A1 3 C 4 MC, M = Ti, Zr, Hf, Ta, W, Mo (sodium chloride) W 2 C, Mo 2 C Compounds of the elements of the later transition Groups, e.g. M 3 C where M = Fe, Mn, Ni MC 2 , M = Ca, Sr, Ba: structure related to NaCl (Fig. 5.13) ThC 2 and MC 2 for M = lanthanide element. Structure (Fig. 17.19) also related to sodium chloride. Li 4 C 3 , Mg 2 C 3 and Ca 3 Cl 2 C 3 all contain C 3 ~ ions. C=C bond length = 134.4 pm, angle at C = 169-176°. Cr 3 C 2 .-C-C-C- chains running through a metal lattice, compare FeB (i) 'Graphite oxide' from the action of strong oxidizing agents on graphite. C:0 ratio is 2:1 or larger and the compounds contain hydrogen. C=0, C-OH and C-O-C groups have been identified. (ii) 'Graphite fluoride' from the reaction with F 2 . White, idealized formula is (CF) m with n about 1.1. The C atoms within the sheets are bonded to one F, while the sheet edges are CF 2 units. These species have advantageous properties as high temperature lubricants. (i) Large alkali metal compounds of K, Rb, or Cs, e.g. C 8 K. The metal is ionized and the electron enters the n system, while the metal ions are held between the sheets. (ii) Halogen compounds. X" ions are held between the sheets and positive holes are left in the n system which increase the conductivity 449 © Pb O O

FIG. 17.2 0 The structure of Pba0 4 . The structure contains

Pb' v 06 octahedra linked together into chains by sharing edges.

These chains are, in turn, linked by Pb"0 3 pyramidal units which both link two of the Pb lv chains and form a chain of Pb"0 3 units 17.5.2 The IV state The IV state is found for all the elements of the Group, and is stable for all but lead. Its properties are well illustrated by the oxygen and halogen compounds. The oxygen compounds are listed in Table 17.10. All the dioxides are prepared by direct reaction between the elements and oxygen. They are also precipitated in hydrated form (except C0 2 of course) by addition of base to their solutions in acid. No true hydroxide, M (OH) 4, exists for any of the elements. The very marked effect of p^-p^ bonding on the structures of the carbon, as compared with the silicon, compounds is obvious, as is the tendency towards a higher co-ordination number to oxygen for the heavier elements. Carbonic acid, H 2 C0 3 , was long thought to be a 'nonexistent' compound, but was recently synthesized at low temperatures by high energy irradiation of C0 2 /H 2 0 mixtures. Free carbonic acid is surprisingly stable, but in the presence of water, its stability dramatically decreases. This is consistent with the observation that carbon dioxide dissolved in water is largely weakly hydrated C0 2 , with only a small proportion (ca. 0.2%) existing as carbonic acid. However, because of the well-known equilibrium H 2 C0 3 -HC0 3 - + H+ solutions of CO 2 in water are acidic. The surprising stability of carbonic acid when prepared under special conditions suggests that other 'nonexistent' acids such as H 2 S0 3 should also be reinvestigated. The protonated carbonic acid molecule, C(OH)J has recently been prepared as its AsFi~ and SbFi~ salts, but these are only stable at low temperatures, decomposing to C0 2 and H + MFi~ at about — 10°C. The oxyanions are also listed in Table 17.10 and comprise a wide array of compounds because of the strong tendency to form condensed polynuclear species based on E0 4 coordination for E = Si, Ge (compare silicates, Section 18.6) or E0 6 units for the heavier elements. While the naturally occurring silicates tend strongly towards ring, sheet, and three dimensional structures, use of different counterions may give alternative structures. It is perhaps significant that the first short chain silicate (Si 4 Oi 3 ) 10 ~ was recently isolated as the Ag + salt. The formation of the heavier chalcogenides also reflects the relative stabilities of the II and IV states. While Si, Ge and Sn form such compounds as GeS 2 or SnSe 2 , there are no such compounds of lead. Among the interesting complex species (again underlining the IV state stability) are Sn 2 Te¿~ (two tetrahedra sharing an edge) and Si 2 Seg~ where the apparently anomalous oxidation state arises from a Se-Se bridge which links two SiSe 3 units, completing a tetrahedron at each Si. All the tetrahalides, MX 4 , are found except for lead (IV) which is too oxidizing to form the tetrabromide or iodide. All may be made from the elements, from the action of hydrogen

halide on the oxide, or by halogen replacement. All the carbon tetrahalides, all the chlorides, bromides and iodides, and also SiF 4 and GeF 4 , are covalent, volatile molecules. The volatility and stability fall in a regular manner with increasing molecular weight of the tetrahalide. By contrast, SnF 4 and PbF 4 , are involatile solids with melting or sublimation points at 705°C and 600°C respectively. They have polymeric structures based on MF 6 octahedra, with partially ionic bonding, as has aluminium trifluoride. Thus the tetrafluorides of the carbon Group parallel the trifluorides of the boron Group in changing from volatile to involatile and polymeric, but the changeover comes further down the Group. Bond lengths are given in Table 2.1 Ob. Carbon tetrafluoride (and all the fluorinated hydrocarbons) and carbon tetrachloride are very stable and unreactive, though CC1 4 will act as an oxidizing and chlorinating agent at higher temperatures. Carbon tetrabromide and iodide are stable under mild conditions, but act as halogenating agents on warming, and are also decomposed by light. The silicon tetrahalides, except the fluoride, are hydrolysed rapidly to 'silicic acid' which is hydrated silicon dioxide. The heavier element tetrahalides also hydrolyse readily, but the hydrolysis is reversible and, for example, GeCl 4 can be distilled from a solution of germanium (IV) in strong hydrochloric acid. A very wide range of 6-coordinate complexes MX 4 .2D is formed by the tetrahalides, and 5-coordinate species such as R^SnX^ (n = 1, 2, 3) are also well known. The latter have a trigonal bipyramidal structure. Seven-coordination is found in Me 2 Sn(NCS) 2 (terpy) where

450 the 3 nitrogens of the terpy (see Appendix B) and the two NCS groups form an almost regular pentagon with the methyls on the axis completing a pentagonal bipyramid. Eight-coordinate lead is found in (C 6 H 5 ) 2 (CH 3 COO) 3 Pb~. The structure is a hexagonal bipyramid with the phenyl groups on the axis and the three bidentate acetates lying in the central plane. 17.5.3 Hydride and organic derivatives Hydride halides of the types MH 3 X, MH 2 X 2 and MHX 3 are also formed. Most representatives of these formulae (for X = F, Cl, Br, I) are found for silicon and germanium, but a few tin compounds, such as SnH 3 Cl, are also known. Such compounds are key members of synthetic routes to organic and other derivatives, as in reactions such as: SiH 3 Br + RMgX or GeH 3 I+AgCN> RSiH 3 (R = organic radical) •GeH 3 CN + AgI

TABLE 17.1 0 Oxygen compounds of carbon Group elements

Compound Dioxides C0 2 Si0 2 Ge0 2 Sn0 2 Ph0 2 Proportion Mo

Pb0 2 Properties Monomer, weak acid Involatile, weak acid Amphoteric Amphoteric Inert to acids and bases Structure Linear, 0=C=O 4:2 coordination with Si0 4 tetrahedra (see Fig. 5.4b) Two forms: one with a 4:2 silica structure, and one with the rutile (6:3) structure Rutile structure Rutile structure Notes PTJ-PT, bonding between first row elements giving Ti-bonded monomer There is some weak p<sup>^</sup>-d<sup>^</sup> bonding in some Si-O-Si systems, though not in the oxide. The Ge/O radius ratio is on the borderline between 6- and 4-coordination Strongly oxidizing

Other oxides (excluding monoxides)

C 3 0 2

Pb 3 0 4

Oxyanions

Carbonate

Silicates

Germanates

Stannates 1 \_ .^,^2

Plumbates} e g M (゜H^

Oxyhalides

Carbonyl halides

COF 2

COC1 2 (phosgene)

COBr 2 Other mixed Carbon suboxide, prepared by dehydrating

malonic acid CH 2 (COOH) 2 p \_^o=c=c=c=o 300°C Red lead: oxidizing, contains both Pb(IV) and Pb(II) coi~ Wide variety (Section 18.6) Variety of species b.p. -83°C Stable Fumes in air Linear, C-C and C-0 distances are intermediate between ti\_jse expected for single and for double bonds Figure 17.20. The structure consists of Pb IV 0 0 octahedra linked in chains the chains are joined by pyramidal Pb n 0 3 groups Planar with n bonding Formed from Si0 4 units Contain both Ge0 4 and GeO 6 units Contain octahedral M0 6 units X ∖ All are planar C = O ^ The molecule contains extended n bonding of the same type as in CO 2 . j Again C and O give p^ bonds Compare the two forms of germanium dioxide Rapidly hydrolysed Very poisonous: has been used as nonaqueous solvent oxyhalides such as ClC(0)Br and FC(0)C1 are known. The C1CO + cation can be stabilized in the solid state by the Sb 3 Fr ó anión.

Silicon oxyhalides

These are all single-bonded species containing -Si-O-Si-Ochains (for example, Cl 3 Si-(OSiCl 2 -) n OSiCl 3 with n = 4, 3, 2, 1 or 0) or rings

(for example (SiOX 2 ) 4 where X = Cl or Br)

Organotin and organolead compounds have

been studied for their pharmaceutical and

biocidal properties and organogermanium com

pounds may have similar properties. Butyl-tin

compounds find widespread use in marine anti

fouling paints but concerns about the accumu

lation of organo-tin in the environment is leading

to a search for alternatives. A number of organo

tin complexes show promising anti-tumour

activity. Tetraethyl lead is manufactured on a

large scale as an anti-knock agent for petrols,

though it is being reduced in usage. It has recently been discovered that the higher hydrides of silicon and

germanium behave similarly, and all the compounds M 2 H 5 X, for M — Si or Ge, and X = F, Cl, Br and I, have been prepared. The elements from silicon to lead have an extensive organometallic chemistry and a wide variety of MR4 and M 2 R 0 compounds exist, with G metal-carbon bonds of considerable stability. All the tetraalkyl and tetraaryl compounds are stable, although stability falls from silicon to lead and the aryls are more stable than the alkyls. For example, tetraphenylsilicon, Ph 4 Si, boils at 530°C without decomposition, tetraphenyllead, Ph 4 Pb, decomposes at 270°C, while tetraethyllead, Et 4 Pb, decomposes at 110°C. A wide variety of organocompounds, with halogen, hydrogen, oxygen or nitrogen linked to the metal, is also known and this class includes the silicone polymers. These are prepared by the hydrolysis of organosilicon halides: R 2 SiCI 2 H 2 O R R R li O S i O S i O - 1 R This long-chain polymer is linked by the very stable silicon-oxygen skeleton and the organic groups are also linked by strong bonds so the polymer has high thermal stability. The organic groups also confer water-repellent properties. The chain length is controlled by adding a proportion of R 3 SiCl to the hydrolysing mixture to give chain-stopping -OSiR 3 groups, while the properties of the polymer may also be varied by introducing cross-links with RSiCl 3 : R 2 SiCI 2 + R 3 SiCI + RSiCI 3 H w « n y 3Í I H2 \* R S I O S I O S I O S I O-SI- C R O R R R R—Si—R O The elements from silicon to lead use their d orbitals to form 6-coordinated complexes which are octahedral. All four elements give stable MF¿~ complexes with a wide variety of cations. The JVICI^" ion is formed for M = Ge, Sn and Pb, and tin also gives SnBr¿~ and Snl¿~. In addition, a variety of MX 4 L 2 complexes are formed by the tetrahalides with lone pair donors such as amines, ethers or phosphanes. The chemistry of the tin compounds is particularly well explored, and both cis and trans compounds are known. When stannic chloride was reacted with phosphorus pentachloride, Cl~ transfer took place (compare PC1 5 itself, Section 17.6.2) to yield (PC1|) 2 SnCl6~, and the mixture also yielded Sn 2 Cli 0 (with a structure involving two octahedra sharing an edge) and SnClJ (trigonal bipyramid). Sixcoordinate complexes may also be formed by the organic derivatives of Ge, Sn and Pb, as long as there are enough electronegative substituents to give reasonable acceptor power. Thus we find Me 2 SnCl4~, and Me 4 Sn 2 Ci5~, each with octahedral Sn and trans Me groups, and the latter with two bridging Cl. There are a much more limited number of 5-coordinated species including MF^ for M = Si, Ge or Sn, and MC1J for Ge and Sn. The chlorides are trigonal bipyramids, as expected, as are the fluorides in the presence of large cations. However, with smaller

cations the fluorides form a cis fluorine-bridged polymeric structure. The d orbitals are also used in internal n bonding, especially in silicon compounds. The classic case is trisilylarnine, (SiH 3 ) 3 N, Fig. 17.21. This has a quite different structure from the carbon analogue, trimethylamine, (CH 3 ) 3 N, shown in Fig. 17.22. The pyramidal structure of trimethylamine is similar to that of NH 3 and reflects the steric effect of the H 3 Si , »N SiH 3

FIG. 17.2 1 The structure of trisilylamine, (SiH 3 ) 3 N H 3 C;

FIG. 17.2 2 The structure of trimethylamine, (CH 3 ) 3 N

An alternative, and increasingly favoured, view

of the bonding in compounds such as trisilyla

mine is that d orbitals play only a relatively

minor role. Instead, interaction between the

filled nitrogen p orbital and a a antibonding Si-H

orbital occurs, i.e. n^cr\*(SiH). FIG. 17.2 3 n bonding in trisilylamine unshared pair on the nitrogen. The NSi 3 skeleton, by contrast, is flat and the nitrogen in trisilylamine shows no donor properties. This is due to the formation of a n bond involving the nitrogen p orbital and d orbitals on the silicon, as shown in Fig. 17.23. The lone pair electrons donate into the empty silicon d orbitals and become delocalized over the NSi 3 group, and hence there is no donor property at the nitrogen. Structural evidence comes from the infrared and Raman spectra and from the zero dipole moment. Although trisilylamine is a gas at room temperature, it has recently been possible to carry out an X-ray study of the solid at low temperatures and this has confirmed the planar Si 3 N skeleton. It is noteworthy that N(CF 3 ) 3 is nearly planar (CNC = 118°) and N(C 2 F 5 ) 3 even closer (CNC = 119.3<sup>°</sup>) showing the effect when strongly electron-withdrawing ligands remove much of the lone pair electron density. Tetrasilylhydrazine, (SiH 3 ) 2 NN(SiH 3 ) 2 , also shows differences in symmetry compared with the methyl analogue, arising from similar n bonding. Another clear case is the isothiocyanate, MH 3 NCS. Where M = C, the C-N-C-S skeleton is bent at the nitrogen atom due to the steric effect of the nitrogen lone pair while, when M = Si, the Si-N-C-S skeleton is linear and there is d^-p^ bonding between the Si and N atoms. Similar effects are

observed in M-0 bonds: dimethyl ether, CH 3 OCH 3 , has a C-O-C angle of 110° which is close to the tetrahedral value, while the bond angle in disilyl ether, SiH 3 OSiH 3 , is much greater—140° to 150° indicating delocalization of the nonbonding pairs on the oxygen. This formation of n bonds using metal d orbitals and a p orbital on a first row element is most marked in the case of silicon, but there is some evidence that it occurs in germanium compounds as well. For example, the Ge-F bond in GeH 3 F is very short, which may indicate d^-p^ bonding but GeH 3 NCO and GeH 3 NCS have bent Ge-N-C skeletons in contrast to their silicon analogues. Other evidence for n bonding by germanium is indirect and derived from acidities and reaction rates in substituted phenylgermanes. 17.5.4 The II state The II state is the stable oxidation state for lead, and the IV state of lead, like thallium (III) in the last Group, is strongly oxidizing. Pb 2+ ions exist in a number of salts, though hydrolysis occurs readily in solution: Pb 2+ + 2H 2 0 ^ PbOH + + H 3 0 + and a further equilibrium is found: 4Pb 2+ + 12H 2 0 ^ Pb 4 (OH)o + + 6H 3 0 + A considerable variety of lead(II) salts is known, and these generally resemble the coresponding alkaline earth compounds in solubility, e.g. the carbonate and sulfate are very insoluble. The halides are less similar and PbCl 2 is, like T1C1, insoluble in cold water though more soluble in hot water. Addition of alkali to lead(II) solutions gives a precipitate of the hydrated oxide, which dissolves in excess alkali to give plumbites. The hydrated oxide may be dehydrated to PbO, called litharge, which is yellow-brown in colour. The structure of PbO is an irregular one in which the lead is coordinated to four oxygen atoms at corners of a trigonal bipyramid, with the fifth position occupied by an unshared pair of electrons. Just as lead forms the mixed oxidation state oxide (see Table 17.10), a mixed oxidation state oxyanion species is formed in compounds like KPb0 2 . In a related example, KNa 7 [Pb0 4 ] [Pb0 3 ], a crystal structure shows an approximately tetrahedral Pb(IV)04~ ion and a pyramidal Pb(11)03" ^ on - Another interesting structure is found in the PbsO® 4 " cluster ion whose core is a cubane Pb 4 0 4 unit with a further Pb bonded to each 0 corner, so that these 4 Pb atoms transcribe a tetrahedron around the cubane. Lead forms all the heavier chalcogenides, PbE, as do Ge and Sn (E = S, Se, Te). Where known, the structures are layer lattices. The II state of tin is mildly reducing but otherwise resembles lead(II). In solution, Sn 2+ ions hydrolyse as in the first equation for Pb 2+ above. Addition of alkali to stannous solutions precipitates SnO^H 2 0 (neither Sn(OH) 2 nor Pb(OH) 2 exist), and the hydrated oxide dissolves in excess alkali to give

stannites. Dehydration gives SnO, which has a similar Stannite is formally named oxostannate(ll) 17.4 THE CARBON GROUP, m np 453 The divalent Si(ll) halides, SiX 2 (X = F, CI, Br and I), can be prepared as reactive species and have angular molecules. For example, SiBr 2 shows a Br-Si-Br angle of 103°, and Sr-Br bond distances of 224 pm. Liquid SiCI 2 is a viscous mixture of polymers in which [SiCI 2 ] n rings have been identified for n = 4, 5 and 6. Sublimation of the tetramer gives an extremely air-sensitive linear polymer with Si-Si = 241 pm and a SiSiSi angle of 114°. These R 2 M species are termed silylenes, getmylenes, stannylenes and plumbylenes for Si, Ge, Sn and Pb, respectively. R R \*\^-N E = C, Si or Ge T \ R = e.g. fert-butyl l| F : R\* = H, Me R^N R FIG. 17.2 4 Structure of stabilized carbene, silylene and germylene species structure to PbO. One stannite structure is known. K 2 Sn 2 0 3 is built of trigonal pyramidal Sn0 3 units with Sn-O-Sn bridges. Tin(II) gives all four

dihalides and a number of oxysalts. In the vapour phase, SnCl 2 exists as monomeric molecules with the V-shape characteristic of species with two bonds and one lone pair. One molecule of water adds to this molecule to give the pyramidal hydrate, SnCl 2 .H 2 0. SnF 2 has a tetrameric structure based on an Sn 4 F 4 puckered 8-membered ring. The Sn-F-Sn bridge angles are 135°, the SnF distances average 215 pm, and each Sn also carries external F with a 207 pm bond length. The Sn atom is thus at the apex of a trigonal pyramid with FSnF angles of 84°. Much longer Sn-F bridges of about 290 pm link these 8-membered rings together. Germanium in the II state gives a number of compounds; GeO, GeS and all four dihalides are well established. These compounds all appear to have polymeric structures and are not too unstable, probably because attack on the polymeric molecules is relatively slow. The known structures are those of GeI 2 , which has the CdI 2 layer structure, and of GeF 2 which has a long-chain structure similar to that of Se0 2 . The II state is readily oxidized to the IV state: thus the dihalides all react rapidly with halogen to give the tetrahalides, while the corresponding reaction of tin(II) compounds is slow. Yellow GeI 2 disproportionates to red GeI 4 and germanium on heating. The divalent compounds are involatile and insoluble, in keeping with a polymeric formulation. One complex ion of the II state is known, GeCl^, in the well-known salt CsGeCl 3 and adducts R 3 P.GeI 2 are also reported. The GeBrJ ion has been characterized as the Rb + salt. The structure shows a pyramidal ion (Ge-Br = 253 pm, BrGeBr = 95.5°) which is more weakly linked to three Br of other ions (Ge- • -Br = 324 pm) giving distorted octahedral geometry at Ge. Germanium(II) may also be obtained in acid solution, in the absence of air, and addition of alkali precipitates the yellow hydrated oxide, GeOj<:H 2 0. Tin and lead form more complexes in the II state than does Ge, though fewer than in the IV state. Halogen complexes, MX^, are pyramidal monomers for the heavier halides while polymeric forms are found for X = F. Thus SnFj" is an infinite chain of SnF 4 square pyramids with Sn at the apices and linked by sharing F atoms at trans corners. Similarly, MOX or M(OH)X 2 compounds are polymers, all with sterically active lone pairs. Cation complexes MX + are also polymers. Formally divalent organometallic compounds R 2 M are mostly ring or long-chain species with M-M bonds, where M = Si, Ge or Sn (see above). Rings with 4, 5 and 7 Si, Ge or Sn atoms are relatively more stable than their carbon analogues. However, simple molecular R 2 M species are known to be highly reactive species which can be trapped in matrices and studied. These divalent organic derivatives, especially of Si, Ge or Sn, are also proven as reaction intermediates. A few examples have been more fully characterized. Large ligands are necessary to allow stable solids, as in the trifluoromethylphenyl compound [(CF 3 ) 3 . C 6 H 2 ] 2 Sn, where the CSnC bond angle is 98°. The corresponding lead compound is also known and has CPbC = 94<sup>°</sup>. Similarly, carbenes such as CC1 2 are well known in organic chemistry and provide a route for the synthesis of cyclopropanes, by the addition to alkenes. The use of large ligands allows stable compounds to be isolated and

compounds like Ge[CH(SiMe 3 )] 2 or Sn[N(CMe 3 )] 2 are monomers. In a series of recent reports, a number of stabilized carbenes, silylenes and germylenes (shown in Fig. 17.24) have been described which show extraordinary thermal stability, a property not expected for such reactive species. The silylene is stable for at least four months at 150°C. This stability has opened up the debate on the electronic structure of such species, and whether or not they are true carbenes, silylenes or germylenes. It is likely that the lone pairs on the nitrogen atoms of such species are donating electron density to the electron deficient carbon, silicon or germanium atom. It has even been suggested that these species are aromatic in nature, due to the possibility of having six Ti-electrons (two from the C=C double bond, and two from each of the nitrogens), similar to benzene. (C 5 H 5 ) 2 M (M = Ge, Sn, Pb) are monomers in the gas phase with ring-M-ring angles about 145<sup>°</sup> and the lone pairs pointing away from the rings. In the solid, they are polymeric. With the very bulky substituent in [Ph 5 C 5 ] 2 Sn the rings are planar and parallel (compare Fig. 16.7). A few mixed species, RMX, RM(OH) or (RM) 2 0 are found. All are polymeric structures with sterically active lone pairs. CHAPTER 17 Although the monomers in the II state have a lone pair, and thus could act as donors (Lewis bases), such behaviour is much rarer than the acceptor modes above. One case is that of (RNM) 4 .2A1C1 3 (for M = Ge or Sn and R is the bulky CMe 3 group) where the M 4 N 4 skeleton is a cubane (with R on N) and two of the four M atoms form donor bonds to A1C1 3 groups. 17.5.5 Reaction mechanisms of silicon Work on inorganic reaction mechanisms is less developed than the corresponding area in organic chemistry, mainly because of the large variety of systems and of experimental difficulties. In particular, many nonorganic reactions are extremely fast. Of all the p elements (for mechanisms at d elements, see Section 13.9), silicon presents one of the most favourable cases for study, and we illustrate something of what is known about Main Group mechanisms by this outline of mechanisms at silicon. Mechanisms are postulated (and remember that all reaction mechanisms are only hypotheses) on the basis of reaction kinetics, and study of silicon has the major advantage that kinetic work may be independently supported by evidence from optically active compounds. The isolation and resolution of active silicon species has given a powerful tool which has been used, particularly by Sommer and his colleagues, to study mechanisms of substitution. A number of optically active silicon species have been reported, one of the first being Ph(a-Nt)(Me)SiX, where a-Nt = a-naphthyl. This was resolved using X - (-)menthoxide (menthol being a naturally

occurring optically active species) by re crystallization from pentane at -78°C. We shall abbreviate the optically active species as R 3 Si\*X. This isolation was greatly aided by the presence of bulky aromatic groups which reduce the rate of reaction. Even so, R 3 Si\*X commonly reacts about a thousand times faster than similar carbon compounds. It was first shown that stereospecific substitutions did occur by cycles of changes analogous to the Walden cycle, e.g. (+)R 3 Si\*H + C1 2 -» (-)R 3 Si\*Cl L -^ 4 (-)R 3 Si\*H [a] D values: +34° -6° -34° Thus one of these steps must occur with inversion, and one with retention, and both must be highly stereospecific. Later work showed that the same relative configuration occurred in the following species R 3 Si\*X, shown with the rotations X H Cl OH OMe Br F [a] D +34° -6° +20° +17° -22° +47°. Thus, the chlorination above is retention, while the reduction involves inversion of configuration. These observations establish that stereospecific substitutions do take place. Extensive further work has led to the postulation of four main mechanisms at silicon. These are briefly outlined. S N 2. This is similar to the mechanism at carbon, but is much faster. It is found for R 3 Si\*X in polar, but poorly ionizing, solvents and particularly when X is a halogen. The reaction takes place with inversion of configuration, and is postulated to proceed through a trigonal bipyramidal intermediate conformation, in which the organic groups are in the central plane M Me Me Ph/ Nt – Nt -SL \""'i \>h Nt Typical examples are hydrolyses, or other replacements of Si-X by Si-OR, and the formation of the hydride above. The addition product between SiH 3 Cl and dimethyl ether can be considered to be a model for the intermediate formed in hydrolysis reactions; the unreactive

Polymetal clusters such as Sn|~ are discussed

in Section 18.4. Y YYX X 17.4 THE CARBON GROUP, ns np 455

FIG. 17.2 5 The structure of the adduct SiH 3 CI[0(CH 3 ) 2 ]

formed from SiH 3 CI and dimethyl ether 0-CH 3 groups prevent any further reaction in the case of the reactive 0-H groups. The structure, Fig. 17.25, has been found to be the expected trigonal bipyramid. While such a process is assisted by using one of the silicon d orbitals to achieve 5-coordination (which probably accounts for the speed of reaction) it does not necessarily follow that a stable intermediate forms. This could happen, or the effect of the d orbital may simply be to lower the activation energy compared with the carbon analogue. S N i. When X = OR, and hydride or organometallic reagents are used in nonpolar solvents, a slow reaction is found which proceeds with retention of configuration. This cannot be S N 2, as the intermediate would undergo fast loss of H or R (leading to racemization) rather than undergo cleavage of the very strong Si-0 bond. It is therefore postulated that the reaction proceeds via a four-centre intermediate, and it is termed internal nucleophilic substitution. The intermediate may be represented as shown, where E is the electrophilic and N the nucleophilic part of the reagent. Thus, for a Grignard reagent, N = R, and E = MgX; or for AlH^, N = H and E=A1H 3 . The process may be understood as a nucleophilic attack assisted by the electrophilic coordination to oxygen which helps to overcome the strong Si-0 binding energy. As an example, R 3 Si\*OMe + LiAlH 4 10h ) R 3 Si\*H [a] D = 16° [a] D - 30° (90% retention) A similar four-centred mechanism is postulated for the very wide range of reactions called hydrometallations in which an M-H bond adds across a double bond. These are found for many metals, M, of which the most important are for M = B, Al (see last section), Si or Sn. S N L This is less common than in carbon chemistry, and is found typically for halides in polar solvents of high dielectric constant. Thus, while R 3 Si\*Cl is recovered unchanged from solution in CC1 4 or an ether, when it is dissolved in acetonitrile or nitromethane (CH 3 CN or CH 3 N0 2 , both with high dielectric constants) racemization takes place rapidly. This has been postulated to proceed through a solvent-stabilized silyl cation, RR'R"Si + (solv). The silyl cation is analogous to the carbonium ion RR'R"C + known in organic chemistry. In fact, the search for the tricoordinated and unsolvated silyl cation is an ongoing area of activity. Since the silyl cation RR'R^Si 4 " is a highly reactive species, it tends to coordinate a 'ligand', either the solvent or the anión itself. Accordingly, the search for the free silyl cation has been paralleled by the search for the least coordinating anión. Classical non-coordinating anions, such as ClO^,BF^, PF¿ and CF 3 SCC, for example, have all been found to coordinate to metals in all parts of the Periodic Table. The use of the even more poorly coordinating anions B(C6F 5 ) 4 and carboranes, e.g. CB 9 Hf 0 , which have their negative charges spread over a large number of atoms, has allowed the isolation of compounds which contain an even weaker, but still persistent, interaction between the R 3 Si + ion and the anión or the solvent. One example is the compound [(toluene)SiEt 3 ] + [B(C 0 F 5 ) 4 ]~ which contains an interaction between the toluene solvent molecule and the silicon atom. Other poorly coordinating anions, such as [B(OTeF 5 ) 4 ]~ and [Nb(OTeF 5 ) 6 ]~ which have their

negative charge delocalized over a large number of electronegative fluorine atoms, also reduce the potential for these anions to act as 'ligands' towards Si + and other reactive species. The use of anions of this type in the isolation of silver carbonyls is described in Section 15.9.1. EO (expanded octet). One special mechanism is sometimes involved when X = F. For most reactions, fluorides behave as other halides and give the above mechanisms. However, the Si-F bond is much stronger than, for example, Si-Cl and this allows a further mechanism. An example is the reaction in which R 3 Si\*F is racemized in dry pentane solution by the addition of MeOH. This reaction has the following characteristics which exclude any of the three mechanisms outlined above: (a) the rate is retarded in formic acid, a solvent of high dielectric constant, hence the reaction is not S N 1. Further, addition of HF retards the reaction so that the reaction does not proceed by loss of F~ as this would be stabilized as HF^. (b) A mixture of R 3 Si\*F and R 3 Si\*OMe plus MeOH gives unchanged R 3 Si\*OMe and racemic R 3 SiF. Thus the racemization is not via R 3 SiOMe or any species which could give rise to it, excluding S N 2 and S N i. CHAPTER 17 Me R∖ R 1 R" N ;E These features led to the postulate of an expanded-octet mechanism with a 5- or 6-coordinate intermediate formed by addition of OMe, and which subsequently loses OMe again: F OM e OMe -R" n OMe As the intermediates are labile or inactive, racemization occurs. There is no breaking of the very strong Si-F bond. Formation of an expanded octet would be assisted by the presence of the fluorine substituent. Note that this mechanism must be rare or there could be no isolation of optically active silicon compounds at all. These conclusions from optical studies may be supported by kinetic studies in favourable cases. Thus, the formation in a fast step of a relatively stable intermediate, followed by a slow dissociation to products A + X-Y fa ^ A-X-Y Sl °-^ 2 A-X + Y would be characterized by a dependence on k 2 alone, and by the fact that the rate of consumption of A was not equal to the rate of appearance of Y. Thus, in S N i, EO and some S N 2 reactions (if the intermediate was relatively long-lived) the above difference in rates would be detected. Conversely, if the intermediate was unstable and immediately gave the product (i.e. if the second step above was very fast) the rate of appearance of Y would equal the rate of loss of A, and k∖ would be rate-determining. This reaction would thus be second order. Such kinetics would characterize the normal S N 2 reaction. Finally, the S N 1 reaction is first order and the determining step is the dissociation into cation and anión. While many mechanisms give rise to an intermediate kinetic

picture (there may be a wide range of lifetimes for the A-X-Y intermediate, for example) if kinetic and optical studies agree, the postulated mechanism is quite strongly supported. As far as the silicon mechanisms outlined above are concerned, such kinetic studies as are reported do validate the proposed mechanisms. 17.6 The nitrogen Group, ns 2 np 3 17.6.1 General properties Of these elements, nitrogen and bismuth are found in only one form while the others occur in a number of allotropie forms. Nitrogen exists only as the triply bonded N 2 molecule, and bismuth forms a metallic layer structure shown in Fig. 17.28. There are a number of

elements which have occurred in the earlier part of the (Section 14.2), and nitrogen complexes in Sections

book include: 15.6 and 16.10. Polynuclear P and As species are

lonization potentials Table 2.8 covered in Section 18.3, the biological role of NO in

Atomic properties and Section 20.1.3 and phosphates in detergents in electron configurations Table 2.5 Section 20.3.1.

Radii Table 2.10, Table 2.11 . Table l7 ' 1 } ^ s some of .^ e Properties of the

™ . . . T t.1 o i / elements and the variation with Group position of

Electronegatm ,es Tab e 2.14 important parameters is shown in Fig 17.26. The

Redox potentials Table 6.3 oxidation free energy diagram is shown in Fig. 17.27.

Structures Chapters &j & 5

TABLE 17.11 Properties of the nitrogen Group elements -15.0 1 14. 0 2 o 13.0 I? 12 ' 0 .2 10. 0 | 9. 0 8.0 As Sb Bi 457 Element Nitrogen Phosphorus Arsenic Antimony Bismuth Symbol N P As Sb Bi Oxidation states -III, III, V (-III), (I), III, V III, V III, V m, (V) Coordination numl 3,4 3, 4, 5, 6 3, 4, (5), 6 3, 4, (5), 6 3,6 1er Availability Common Common Common Common 1Î  $\partial X^{\circ}$  \*'\* <fi f i!f .r- (0 C fl\* \*1 = "5 - A N P A s S b B i FIG. 17.26 Some properties of elements of the nitrogen Group 6.0 h 5.0 4.0 >, 3.0 LU CD 2.0 1.0 0.0 -1.0 -2.0 -As -III -I I I 0 I I I II I I V oxidation state FIG. 17.2 7 Oxidation state free energy diagrams of elements of the nitrogen Group. This is the most complex oxidation state diagram of all the Main Groups. The properties of nitrogen are the most individual, with the element and the -III states as the most stable. All the positive states between 0 and V tend to disproportionate in acid solution (though many form gaseous species in equilibrium with the species in solution) and the -I state is markedly unstable. The curves for P, As, Sb and Bi form a family in which the -III state becomes increasingly unstable (values for Sb and Bi in this state are uncertain) and the V state becomes less stable with respect to the III state from P to Bi. All intermediate states of phosphorus tend to disproportionate to PH 3 plus phosphorus(V). The diagram also illustrates the very close similarity between As and Sb and the strongly oxidizing nature of bismuth(V)

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FIG. 17.29 Structures of phosphorus allotropes: (a) white

phosphorus, (b) brown phosphorus, (c) red phosphorus

(postulated) allotropes of phosphorus. In white phosphorus, and also in the liquid and vapour states, the unit is the P 4 molecule where the four phosphorus atoms form a tetrahedron. If the vapour is heated above 800°C, dissociation to P 2 units starts and rapid cooling of the vapour from 1000°C gives an unstable brown form of phosphorus which probably contains these P 2 units. When white phosphorus is heated for some time above 250°C, the less reactive red form is produced. The structure of this form is not yet established and it exists as a number of modifications with various colours—violet, crimson, etc. These might be different structures or due to different crystal sizes, but they may also be due to the incorporation of part of the catalysts used in the transformation. When white phosphorus is heated under high pressure, or treated at a lower temperature with mercury as a catalyst, a dense black form results which has a layer structure like bismuth. A further vitreous form is also reported which results from heating and pressure. The structures of some of these allotropes are shown in Fig. 17.29 and the interconversion of the allotropes in Fig. 17.30. White phosphorus is the most reactive of the common allotropes, red phosphorus is much less reactive, and black phosphorus is inert. Substantial further insight is provided by the recently established structures of the

polyphosphorus hydrides and anions outlined in Section 18.3. Arsenic and antimony each occur in two forms. The most reactive is a yellow form which contains M 4 tetrahedral units and resembles white phosphorus. These yellow allotropes readily convert to the much less reactive metallic forms which have the same layer structure as bismuth. Binary compounds of these elements are similar to those of previous Groups. Nitrides range from those of the active metals, which are definitely ionic with the N 3 " ion, through the transition metal nitrides which resemble the carbides, to covalent nitrides like BN and S 4 N 4 . Heated Ba metal reacts with N 2 giving a product which hydrolyses to give 30% N 2 H 4 and 70% NH 3 . This suggests that the N 2 ~ ion is formed as well as N 3 ~. The phosphides are similar. The interesting polyphosphide ion, P^~, is isoelectronic with C10 2 and contains an unpaired electron. The structure is V-shaped with an angle of 118<sup>°</sup> and a P-P length of 218.3 pm. The heavier elements form compounds with metals which become more alloylike as one passes from phosphorus to bismuth. One important feature is the appearance of ionic nitrides, as compared with monatomic carbides which are not ionic. Ionic nitrides include the Li, Mg, Ca, Sr, Ba and Th compounds. They are prepared by direct combination or by deammonation of the amides: 3Ba(NH 2 ) 2 -^Ba 3 N 2 +4NH 3 By contrast, the corresponding carbides either contain polyanions, like the acetylides, or are intermediate between ionic and giant covalent molecules. brown ^ black FIG. 17.3 0 The interconversion of the allotropes of phosphorus. The reaction conditions are indicated by letters as follows: (a) melting followed by quenching, or vacuum sublimation, (b) heating above 250°C, (c) heating to 220°C under pressure, (d) heating above 450°C, or on prolonged standing at room temperature, (e) at 25°C under high pressure, (f) vacuum sublimation, (g) heating above 250°C under pressure, (h) heating to 400°C under pressure, (i) rapid cooling of vapour with liquid nitrogen, (j) warming above liquid nitrogen temperature (-196°C). Many of these interconversions may also be brought about by catalysis, especially by mercury CHAPTER 17

OCCURRENCE AND USES OF THE NITROGEN GROUP ELEMENTS

Nitrogen gas is now produced on a substantial scale, largely as a byproduct of the isolation of oxygen from air for steelmaking. It is used to provide a cover for processes which are sensitive to air, and as liquid, it is
in ever-increasing use as a coolant. One of the largest manufacturing applications using nitrogen is the Haber process for producing NH 3 from N 2 and H 2 under pressure over an iron catalyst. Recent work on catalysts, such as ruthenium on carbon, allows the reaction to occur at atmospheric pressure and ordin ary temperatures, foreshadowing a cheaper Haber process. The ammonia is used mainly as a fertilizer, as salts, and part is converted to nitrate by catalytic oxidation, again mainly for use as a fertilizer. Hydra zine, N 2 H 4 is used in agricultural chemicals and herbicides and as an intermediate in Pharmaceuticals. Elementary phosphorus, made by carbon reduction of phosphate minerals, is extensively used in matches. The old formulation, based on poisonous white phosphorus, has now been entirely superseded by red phosphorus mixtures which also include sulfides of P and Sb. The oxidant is chlorate, and safety matches have separate oxidant in the match, with the phosphorus species on the striking surface. The major production of phosphorus compounds is that of phosphate fertilizer, mostly using the family of apatite ores, Ca 5 (PO 4 ) 3 X (X = OH, Cl or F). These are of low solubility and superphosphate fertilizer, of higher, solubility, is produced by treatment of the crude phosphate rock with sulfuric acid. Phosphoric acid is produced from the phosphate rock by treatment with sulfuric acid followed by purification by a solvent extraction process (see Section 7.3). Phosphate, especially as a component of DNA and RNA, is essential to all life processes. The major component of teeth and the main bone mineral is hydroxyapatite, accompanied in the bone by amorphous calcium phosphate. In teeth F replacement, giving fluoroapatite, increases toughness and resistance to caries. Phosphates are widely used as food additives (such as phosphoric acid in cola drinks and sodium phosphates in processed foods), as flame retardants and in the prevention of scale and corrosion in water-cooling systems. Phosphorus sulfides are also manufactured on a large scale as starting materials for the synthesis of organophosphorus compounds which are widely used as pesticides, for example malathion. Many of the military nerve gases are organophosphorus compounds, e.g. sarin CH 3 P(O)(OPr J ')F. Traditional uses of arsenic compounds in insecticides and fungicides, e.g. as wood preservatives, are being phased out as less toxic alternatives become available. All three heavier elements find uses in alloys (see under tin in the last section). As and Sb are becoming increasingly important in the IIW semiconductor materials mentioned under gallium above. Sb 2 O 3 finds substantial use, along with various phosphorus compounds, as flame retardants in plastics. Nitrogen, because of the high strength of the triple bond (heat of dissociation = 962 kj moP 1 ), is inert at low temperatures and its only reaction is with lithium to form the nitride. At higher temperatures it undergoes a number of important reactions including the combination with hydrogen to form ammonia (Haber process), with oxygen to give NO, with magnesium and other elements to give nitrides and with calcium carbide to give cyanamide: N 2 + CaC 2 -> CaNCN + C The other elements react directly with halogens, oxygen and oxidizing acids. This Group shows a richer chemistry than the boron and carbon Groups, as there are more than two stable oxidation states and there is a wider variety of shapes and coordination numbers. Nitrogen shows a stable -III state in ammonia and its compounds, as well as in a wide variety of organo-nitrogen compounds. Phosphorus has an unstable III state in the hydride and also forms acids and salts, which contain direct P-H bonds, in the III and I states. In the normal states of V and III a variety of coordination numbers is found. The MX 3 compounds, where M = any element in the Group and X = H, halogen or pseudohalogen, or organic group, are pyramidal with a lone pair on M. The MX 5 compounds are trigonal bipyramids in the gas phase and adopt a variety of structures in the solid. It is interesting that, while PPh 5 and AsPh 5 are

trigonal bipyramids, SbPh 5 is a square pyramid both in the solid and in solution. This is a second (with InCrl") Main Group example of the square pyramid as the alternative five electron pair structure. A number of MXj species are known, as well as MX 3 . A (where A = any acceptor molecule such as BR 3 ) and these are tetrahedral. A few M 11 ^" complexes also exist and these are square pyramids with a lone pair in the sixth position. Finally, a variety of A/HÇ and M V X 5 .A

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TABLE 17.12 Coordination numbers and stereochemistry in

the nitrogen Group Numbe> of elect pairs 4 4 4 5 5 5 : 6 6 r Numb ron of n bonds 0 0 1 0 1 2 0 0 er Number non-bon pairs 0 1 1 0 0 0 0 1 of Shape ding Tetrahedron Pyramid V Bipyramid Tetrahedron Plane Octahedron Square pyramid Examples NH+, MR+, PX+ (X = all halogens) MH 3? MR 3 , MX 3 (X = all halogens) NO^ MF 5 , PC1 5 , PBr 5 , PPh 5 (SbPh 5 — see text) MOX 3? M0^~, HPO^-, H 2 P02 N0 i MFê , PCl 6 7 SbPh 6 SbF^(M = P, As, Sb, and Bi, R= simple alkyl radical, Ph = phenyl) compounds are found which are octahedral. Many of these shapes are repeated in compounds which include n bonding. A full set of examples is gathered in Table 17.12. M-M links for the heavier elements of the Group are found for all elements in the organic compounds R 2 M-MR 2 , although the Bi examples are unstable. The methylarsenic, cacodyl, Me 2 As-AsMe 2 , has been known since 1760. The corresponding hydrides are less

CATENATION IN GROUP is ELEMENTS; HYDRAZINE, THE AZIDE ION AND OTHER NITROGEN-RICH SPECIES

The Group 15 elements show a significant tendency to catenation, if less markedly than does the carbon Group. Polynuclear compounds are discussed in Sections 18.3 and 4. Simpler chain compounds of nitrogen involve both single bonds, as in hydrazine and its derivatives, R 2 N-NR 2 , where R = H, F or organic groups, and multiple bonds as in the diazenes RN=NR (R=F or organic groups, R=H is unstable unless coordinated—see Section 16.10). Nitrogen is found in a chain of three atoms in hydrazoic acid, HN 3 , and in the azides. These are prepared from amide and nitrous oxide: 2NaNH 2 + N 2 O -» NaN 3 + NaOH + NH 3 The azide ion is linear, and isoelectronic with CO 2 . The acid, called hydrazoic acid, is bent at the nitrogen bonded to the substituent, with the NNH angle equal to 114° and the bond distances indicating the presence of single and triple bonds (Fig. 17.3la). Organic azides, RN 3 , have similar structures. In the N^ ion the two N-N distances are equal at 116pm, showing delocalization of the n bonding. The amino diazonium cation, H 2 Nj has been recently prepared and can be thought of as a protonated hydrazoic acid with both hydrogens residing on one nitrogen, and single and triple bonds between the nitrogens (Fig. 17.31D). Bond lengths of 121 pm for the central bond and 143 pm for the outer ones, and angles at the central N of 109°, are found in N 4 H 4 , which is a sublimable solid

containing a chain of 4N atoms, H 2 N-N = N-NH 2 . A few organic derivatives R 4 N 4 are also reported, together with one or two longer chain organic compounds, but all are relatively unstable. N CI 5 W-N" "N WCI 5 The branched chain isomer of tetrazene is reported, where the planar tetrazene completes an octahedron around each W. Only this coordinated form is known, but this is the first example of a branched nitrogen chain. (a) 124pm 113p m (b) 114° 130.5pm 108.8p m 100.8pm FIG. 17.31 Structures of (a) hydrazoic acid, Only one resonance form is shown for each and (b) aminodiazonium cation, CHAPTER 17 461 (a) The N 5 + ion (b) The N 5 - ion The azidopentazole isomer of N 8 (d) The N(N 3 ) 3 isomer of N 10 The oxide N 4 O N O O w «  $\ast$  v\_y v^

Compounds which are extremely nitrogen-rich are

FIG. 17.3 2 Structures of pentoxides, M 2 0 5 , of the elements of

the nitrogen Group: (a) N 2 0 5 , (b) P 4 0 10 monodentate bidentate M— bridging Bonding modes for the nitrate (NO 3 ~) ion from the action of FN0 2 with excess LiN0 3 . The solid is ionized with a planar nitrate ion and a linear nitronium cation, NOj. Linear nitronium, or nearly so, is found with other stable anions: in NOjClOj, the ONO angle is 175<sup>°</sup>. In the gas phase, the N 2 0 5 molecule exists with the structure of Fig. 17.32. Higher oxides of nitrogen, N0 3 and N 2 0 6 , have been reported from the reaction of ozone on N 2 0 5 but little is known of them. Phosphorus bums in an excess of air to give the pentoxide which has the molecular formula, P 4 0i 0 , and, in the vapour, the tetrahedral structure shown in Fig. 17.32b. This form is also found in the liquid and solid, but prolonged heating of either gives polymeric forms. Both 12and 20-membered rings of PO 4 tetrahedra linked by comers have been identified. The environments of each phosphorus atom in P 4 O 10 and in the polymeric forms are similar. Each phosphorus atom is linked tetrahedrally to four oxygen atoms, three of which are shared with three other phosphorus atoms, while the fourth link is a P=0. The pentasulfide exists in the same P 4 Si 0 form as the pentoxide (Fig. 17.32b) and the mixed oxide-sulfides P 4 0 6 S 4 (with terminal P=S) and P 4 0 4 S 6 (with terminal P=0), completing a satisfying series of symmetric molecules. P 4 S 9 N~ is also isoelectronic and isostructural, with the N~ in an edge-bridging position. The pentoxides, M 2 0 5 , of arsenic, antimony and bismuth are made by oxidizing the element or the trioxide. Increasingly powerful oxidizing agents are needed from arsenic to bismuth, and Bi 2 0 5 is not obtained in a pure stoichiometric form. As 2 0 5 is a polymeric structure consisting of As0 4 tetrahedra and As0 6 octahedra sharing corners. The structures of Sb 2 0 5 and Bi 2 0 5 are not known but are probably based on M0 6 octahedra like their anions. All three lose oxygen readily on heating to give the trioxides. Oxyacids and oxyanions of the V state are a very important class of compounds in the chemistry of this Group. The nitrogen, phosphorus and arsenic compounds are included in Table 17.13 p.466. Antimony and bismuth do not form acids in the V state. The oxyanions may be made by reaction of the pentoxides in

alkali or by oxidation of the trioxides in an alkaline medium. The bismuthates are strongly oxidizing, the best known being the sodium salt, NaBi0 3 , which is used to identify manganese in qualitative analysis by oxidizing it to permanganate. The antimonates are oxidizing, but more stable than the bismuthates, and are octahedral ions, Sb(OH)i~. This is in contrast to the tetrahedral coordination to oxygen shown in the phosphates and arsenates. Both phosphorus and arsenic form acids in the V state, both the mononuclear acid, H 3 M0 4 , and polymeric acids. The polyphosphoric acids include chains, rings and more complex structures, all formed from PO 4 tetrahedra sharing oxygen atoms. A wide variety of polyphosphate ions also exists, and structures of the first three members are indicated in Fig. 17.36e, f and g p.467. The detailed structure of the fourth member, P 4 OiJ, isolated as the [Co(NH 3 ) 0 ] 3+ salt, shows a significant alternation of P-0 bond lengths in the chain. Tripolyphosphates are used in detergents as they are excellent sequestering agents, though use has diminished as worries about eutrophication have grown (see Section 20.3.1). These pyro-, meta- and other polyphosphates are stable and hydrolyse only slowly to the orthoacid, H 3 P0 4 . Polyarsenates also exist in similar forms, but these are much less stable and readily revert to H 3 As0 4 . Nitrogen in the V state forms nitric acid, HN0 3 , and the nitrate ion, NOJ. Here, the coordination number of only three to oxygen, and the planar structure, reflect the presence <sup>°</sup>f PTT-PK bonding between the first row elements, nitrogen and oxygen. Although usually found as the free anión, nitrate does sometimes coordinate to metals. It occurs as a monodentate, bidentate or bridging ligand. A second, unexpected, anión has recently been reported, NO<sup>^</sup>. A structural study of the sodium salt shows a tetrahedral structure with a NO distance of 139 pm, compared with 122 pm in N0i~ (Fig. 17.33) and 122 pm for N-0 and 141 pm for N-OH in the isolated HONO 2 molecule. The N-O bond order in NO^ is thus near to one, suggesting a relatively weak interaction, and a description in terms of semi-polar bonds is probably the most appropriate, compare Section 18.9. The stable V state halides are limited to the pentafluorides, PF 5 , AsF 5 , SbF 5 and BiF 5 , together with PC1 5 , SbCl 5 and PBr 5 . This reflects the decreasing stability of the V state from phosphorus to bismuth. AsCl 5 has only recently been identified as a product of the UV photolysis of AsCl 3 and C1 2 at -105°C. It decomposes at -50°C. This behaviour is an 463

(a) (b)

(c) P n N=N, 2

FIG. 17.3 3 The structures of some nitrogen oxyanions:

(a) hyponitrite, (b) nitrite (0-N-O angle 116 to 132<sup>°</sup>, N-O

bond length 113 to 123 pm in different salts), (c) pernitrite,

(d) nitrate (N-0 bond length 121.8 pm, 0-N-O angle 120°) example of the 'middle element anomaly' already discussed. All the structures so far determined show that the pentahalides are trigonal bipyramidal in the gas phase/but these structures alter in the solid, reflecting the instability of 5-coordination in crystal lattices. PC1 5 ionizes in the solid to PClJPCC while PBr 5 ionizes to PBr^Br". The cations are tetrahedral and PCC is octahedral. In addition there is another metastable modification of solid PC1 5 which has been found by an X-ray diffraction study to be (PCi;j<sup>~</sup>) 2 (PCC)(Cr), with a significant interaction between the PClJ and Cl~ ions. This form slowly reverts to the normal PClJPCÇ form on standing at room temperature. SbF 5 also attains a more stable configuration in the solid, this time by becoming 6-coordinated through sharing fluorine atoms between two antimony atoms in a chain structure. Except for BiF 5 , all the pentafluorides readily accept F~ to form the stable octahedral anión, MFర~. PF 5 , especially, is a strong Lewis acid and forms PF 5 .D complexes with a wide variety of nitrogen and oxygen donors (D). Antimony also forms the dimeric ion Sb 2 Ff 1 , consisting of two SbF 6 octahedra sharing a corner. The pentachlorides are similar but weaker acceptors. They do accept a further chloride ion, and SbCli~ in particular is well established and stable: PCC is mentioned above. It has recently been shown that AsCl¿~ may also be prepared if it is stabilized by a large cation, thus Et 4 N + AsCC has been prepared. All these pentahalides may be made by direct combination or by halogenation of the trihalides, MX 3 . The pentafluorides, and PC1 5 , are relatively stable, but PBr 5 and SbCl 5 readily lose halogen at room temperature (to give the trihalides) and are strong halogenating agents, as is BiF 5 which is by far the most reactive pentafluoride. A number of mixed pentahalides, such as PF 3 C1 2 , are also known. They are formed by treating the trihalide with a different halogen: PF 3 + C1 2 -> PF 3 C1 2 These are similar to the pentahalides in many ways. For example, PF 3 C1 2 is covalent on formation but passes over into the ionic form PCl^PF^ on standing. Another example is AsF 3 Cl 2 which also appears to be ionized to AsCl|AsF^, showing that the

second ionic component of the unstable AsCl 5 exists. It has also been shown that AsClF 4 is quite stable but that, though AsCl 4 F exists at low temperatures, it readily loses C1 2 to give AsClJ AsFi~ and AsCl 3 . AsCl 3 F 2 is not accessible from AsCl 3 , but results from the treatment of AsCl 2 F 3 with CaCl 2 . Like PC1 3 F 2 , the Cl are equatorial in the trigonal bipyramid. Overall, As(V) with 4 or 5 bonded Cl is unstable with respect to As (III) plus C1 2 , though it can be stabilized by suitable donors or in the presence of suitable counter-ions. The set of AsXj ions was completed by the discovery of Asl| as the A1C1J salt. The cation P 2 lJ, with a P-P bond, has been prepared by reaction of PI 3 with A1I 3 , or by reaction of P 2 I 4 with I 2 and A1I 3 . The cation can be viewed as an analogue of the PIÍ" ion in which an I is replaced by a PI 2 group. Although nitrogen cannot form a pentahalide, as only four valency orbitals are present in the second level, it is interesting that the cation NFj exists showing that nitrogen(V) can bond to fluorine, in a species where only a interactions are possible. The oxychloro cation of nitrogen(V), (NOC1 2 ) + , has been made as the [AsF 6 ]  $^{\sim}$ or [SbCl 6 ]~ salt. The structure is a flattened pyramid with 0-N-C1 =119°. In their covalent forms, the mixed pentahalides PX^Y 5 . n , such as PF 3 C1 2 , have structures in which the most electronegative halogens occupy the two axial positions. Although PH 5 is unknown, mixed hydride-fluorides of P(V), are established e.g. PHF 4 and PH 2 F 3 . These form anions, HPF^ and H 2 PF 4 , related to PF¿~. Nitrogen, in the V state, forms the oxyfluoride NOF 3 from NF 3 and 0 2 or from the elements. It readily transfers  $F^{\sim},$  e.g. to form (NOF 2 ) + (BF 4 )~. The structure is pyramidal: see remarks above about the formulation of H 3 N0 4 . Phosphorus and arsenic form a range of oxyhalides in the V state. Three compounds of phosphorus are known, POX 3 where X -F, Cl or Br, and for arsenic AsOF 3 and AsOCl 3 . POC1 3 may be made from PC1 3 or from the pentachloride and pentoxide: PC1 3 + ±0 2 -> POC1 3 or P 4 Oio + 6PCl 5 -> 10POC1 3 (d) The other phosphorus compounds are made from the oxychloride. AsOF 3 is made by the action of fluorine on a mixture of AsCl 3 and As 2 0 3 while AsCl 3 +0 3 gives AsOCl 3 which decomposes at -30°C. All these are tetrahedral X 3 M=0, with p^-d^ bonding between the 0 and M atoms (Fig. 4.23). Phosphorus gives the corresponding sulfur and selenium compounds, PSX 3 and PSeX 3 , again illustrating the marked stability of 4-coordinated P(V). Three pentasulfides are found in this Group. P 4 S 10 has the same structure as P/tC^o— and there is also a compound P40 6 S 4 which again has the same structure, with the oxygen atoms bridging along the edges of the tetrahedron, and a sulfur

atom attached directly to each phosphorus. The structures of As 2 S 5 and Sb 2 S 5 are unknown. All three sulfides may be formed by direct reaction between the elements, and arsenic and antimony pentasulfides are also formed by the action of H 2 S on As(V) or Sb(V) in solution. PHOSPHONITEILIC HALIDES AND PHOSPHAZENES One final important class of phosphorus (V) com pounds is that of the phosphonitrilic halides. If PC1 5 is heated with ammonium chloride, compounds of the formula (PNC1 2 ) X result: PC1 5 + NH 4 C1 -> (PNC1 2 ) 3 + (PNC1 2 ) 4 + (PNC1 2 ) X + HCl The corresponding bromides may be made in a similar reaction, and the chlorines may also be replaced by groups such as F, NCS, or CH 3 and other alkyl groups, either by substitution reactions, or by using the appropriate starting materials. When x = 3 or 4, the six- or eight-membered rings shown in Fig. 17.34, are formed. Similar rings have been identified for x values up to 17 in the case of chlorides and fluorides and forx = 6 for the bromides. In addition, for large values of x, linear polymers are formed, of accurate formula C1(PNC1 2 ) X PC1 4 . In the ring com pounds, the trimer and pentamer are planar, while the tetramer and hexamer are puckered. The nature of the bonding in the rings, and also in the chain compounds, is not yet clearly determined but prob ably involves n bonding between nitrogen p orbitals

and phosphorus d orbitals. In the trimeric chlorides, it has been suggested that this n bonding involves a strong interaction above and below the plane of the ring, as in benzene, and also a weaker interaction in the plane of the ring. In the nonplanar tetramer, this second type of n bonding can make a stronger contribution. In polymers, with OR groups such as OCH 2 CF 3 replacing the halides, useful properties are found, especially resistance to oxidation and burning. These polyphosphazenes are finding application in

special performance rubbers, gaskets and insulating (a) CI Cl\*\*\*^ CI CI C I (b) CI CI <^N, N CI y ^ ^ N^ \C I cr c i RO OR RO QR RO OR RO OR RO OR \j \î \l \i \î /P\ FIG. 17.3 4 (a) Trimeric and (b) tetrameric phosphonitrilic chlorides (CI 2 PN) n and (c) a polyphosphazene materials. As these polymers are compatible with tissues, they have potential value in biomédical devices. Reference Inorganic polymer, I. MANNERS, Angewandte Chemie 35, 1996, 1602-1621. N o o The structure of N 2 O 3 17.6.3 The III state The III state is reducing for nitrogen, phosphorus, and arsenic, and the stable state for antimony and bismuth. Among the oxygen compounds, all the oxides, M 2 0 3 , and all the oxyanions are known, but the free acids of the III state are found only for nitrogen, phosphorus, and possibly arsenic. This points to an increase in basicity down the Group, as expected. The oxide of nitrogen, N 2 0 3 , is found as a deep blue solid or liquid, melting at about -100°C. It is formed by mixing equimolar proportions of NO and NO 2 , and reverts to these 465 144pm I 128° 164pm 0 p o o FIG. 17.3 5 The structure of P 4 0 7

- (a)
- (b)
- (c)
- (d) 22s? 4(f)
- (9)

phosphite, (b) phosphite, (c) pyrophosphite, (d) hypophosphate,

(e) orthophosphate, (f) pyrophosphate, (g) tripolyphosphate î M Q^P D , two components in the gas phase at room temperature. An X-ray structure determination, carried out at low temperature, showed the compound to be 'nitrosyl nitrite' with an N-N bond. N 2 0 3 , or an equimolar mixture of NO and NO 2 , gives nitrous acid when dissolved in water, and nitrites when dissolved in alkali. Phosphorus (III) oxide results when phosphorus is burned in a deficiency of air. In the vapour phase, it has the formula P40 6 , and a structure derived from that of P 4 0i 0 by removing the terminal oxygen atoms, see Fig. 17.32. The phosphorus (III) oxide is acidic and reducing, and dissolves in water to give phosphorous acid. We note here that there is now a complete series of mixed P(III)/P(V) oxides, P 4 0^ with\*=7 (Fig. 17.35, compare Fig. 17.32b), 8 and 9, where terminal oxygens are progressively added to P 4 0 6 giving all intermediate structures between that and P 4 0i 0 . When arsenic is burned in air, the only product is the trioxide, which has the formula As 406, and a similar structure to P 4 0 6 , in both the gas phase and in the solid. A second form also occurs in the solid, but this structure is not known. Arsenic trioxide is acidic. Antimony and bismuth also burn in air to give only the trioxides. Antimony trioxide has the form, Sb 4 0 6 , both in the gas and in the solid, and there is a second solid form. This has a structure consisting of long double chains made up of • • -0-Sb-O-Sb-O- • • single chains linked together through an oxygen atom on each antimony. Antimony trioxide is amphoteric. Bi 2 0 3 is yellow (all the other compounds are white) and exists in a number of solid forms. These are not known in detail, but some at least contain Bi0 6 units in a distorted prism arrangement. Bismuth trioxide is basic only. Antimony and bismuth, in the III state, commonly exist in solution and in their salts as the M0 + ion, as already noted. The oxyanions and acids of phosphorus (III) and arsenic (III) are included in Table 17.13 and Fig. 17.36. All the structures known contain 4-coordinated phosphorus or arsenic, and the III oxidation state results from the presence of a direct P-H or As-H bond (which, of course, does not ionize to give a proton). Although the stable form of phosphorous acid is the tetrahedral form shown in Fig. 17.36, there is some evidence from exchange studies (compare Section 2.3) for the transient existence of the pyramidal P(OH) 3 form.

Organic derivatives of this form, P(OR) 3 , are well known. Phosphorous acid, and the phosphites, are reducing, and also disproportionate readily as the oxidation state free energy diagram, Fig. 17.27, shows: 4H 3 P0 3 -> 3H 3 P0 4 + PH 3 Arsenites are also mildly reducing with a potential, in acid, of 0.56 V with respect to arsenic (V) acid, so that arsenites are rather weaker reducing agents than iron(II) in acid solution. One interesting bismuth(III) compound is the complex oxycation [Bi 6 0 4 (OH) 4 ] 6+ whose structure contains six Bi atoms in an octahedron with 40 and 40H groups triply bridging the triangular faces in a regular manner. This is formed by Bi 2 0 3 in perchloric acid. Analogous Sn. V and Ce cluster ions of this M 6 0 4 (OH) 4 formula are found. Arsenic, antimony and bismuth all form trisulfides, M 2 S 3 . The arsenic compound exists as As 4 S 0 , while the antimony and bismuth sulfides have polymeric chain structures. All are formed by the action of H 2 S on solutions of the element in the III state. The tale of the lower phosphorus sulfides is more complicated, as the main series have P-P bonds and may be seen as derived from the P 4 tetrahedron. The lowest S content is found in P 4 S 3 (Fig. 17.37a) where S atoms are inserted in three of the six edges of P 4 . The mixed P/As analogue, PAs 3 S 3 has the P at the unique apex position and an As 3 triangle in the base. Further edge insertion is found in the two isomers of P 4 S 4 , where the remaining two P-P bonds are either contiguous or at opposite edges of the tetrahedron. In P 4 S 5 , S is inserted in an edge (Fig. 17.37b), while P 4 S 7 sees edge insertion and terminal addition (Fig. 17.37c). The remaining well-established compound is P 4 S 9 where the structure is like the oxide, with one terminal S removed from P 4 Si 0 (Fig. 17.32b). We note that, as S is isoelectronic with P~ or PH, the species P 7 H 3 and P 7 ~ (and also As 7 ~) have structures analogous to Fig. 17.37a (compare Section 18.2). Arsenic also forms a sulfide, As 4 S 3 , and a selenide, As 4 Se 3 , with the P 4 S 3 structure. A third arsenic sulfide, As 4 S 4 (called realgar], is

#### Nitrogen

The nitrogen acids and anions all show nitrogen 2- or 3-coordinated to oxygen and all (except hyponitrous acid) have p^-p^ bonding between

N and 0.

H 2 N 2 0 2 N 2 0 2 ~ Reduction of nitrite by sodium amalgam. Weak acid. Readily decomposes to N 2 0.

#### hyponitrous hyponitrite

HNO 2 NOi∼ Acidify nitrite solution. Free acid known only in gas phase. Weak acid. Aqueous solution

nitrous nitrite decomposes reversibly, 3HN0 2 - >• HN0 3 + 2NO + H 2 0.

HOONO (OONO)~ H 2 0 2 + HNO 2 . Free acid postulated as reaction intermediate.

Pernitrous Pernitrite

HN0 3 NC>3~ Oxidation of NH 3 from Haber process. Strong acid. Powerful oxidizing agent in

nitric nitrate concentrated solution.

The structures of the anions are shown in Fig. 1 7.33

Phosphorus

The phosphorus acids and anions all contain 4-coordinate phosphorus. In the phosphorus(V) acids, all four bonds are to oxygen, while P-H

and P-P bonds are present in the acids and ions of the I and III states. Various intermediate oxidation states are found in anions which have

P-P bonds, often with P-H ones as well. The most striking :ase is [P(0)(OH)] 6 . The crystal structure of the caesium salt shows a six

membered, puckered, P 6 ring.

H 3 PO 2 H 2 PO2~ White P plus hydroxide. Monobasic acid, strongly reducing.

Hypophosphorous hypophosphite

H 3 P0 3 HP0 3 ~ Water plus P 2 0 3 or PC1 3 . Dibasic acid, reducing.

Phosphorous phosphite

H 4 P 2 0 5 H 2 P 2 05~ Heat phosphite: dibasic acid with P-O-P link. Reducing.

Pyrophosphorous Pyrophosphite

H 4 P 2 0 6 P 2<sup>°</sup>6<sup>~</sup> Oxidation of red P, or of P 2 I 4 , in alkali, gives sodium salt, which gives the acid on

hypophosphoric hypophosphate treatment with H + . Tetrabasic acid with a P-P link. Resistant to oxidation to phosphoric acid.

H 3 P0 4 P0 4 ~ P 2 0 5 or PC1 5 plus water. Stable,

(ortho) phosphoric phosphate

Also pyrophosphate (O 3 POPO 3 ) 4  $^{\sim}$  Formed by heating orthophosphate. Linear polyphosphates with n up to 5 and cyclic

polyphosphates (O 3 P[OPO 2 ] n OPO 3 ) (4+n) ~ metaphosphates with m = 3 to 10 have been individually identified (cf. Fig. 7.2).

metaphosphates (P0 3 )™~

The structures of the phosphorus anions are shown in Fig. 17.36.

Arsenic

H 3 As0 3 ?, or As 2 0 3 .xH 2 0 HAs0 3  $^{\sim}$  and more Formed from the trioxide or trihalides. The acid does not contain As-H and is weak, but complex forms the arsenites are well established in mononuclear and polynuclear forms. The

arsenious acids arsenites arsenic (III) species are reducing and thermally unstable.

H 3 As0 4 As0 4  $^{\sim}$  As + HNO 3 – » H 3 As0 4 .¿H 2 0. Tribasic acid and moderately oxidizing. Arsenates are

arsenic acid arsenate often isomorphous with the corresponding phosphates.

Condensed arsenates A number of these exist in the solid state but are less stable than polyphosphates and rapidly hydrolyse to As0 4 ~.

As far as they are known, arsenic anions and acids have the same structures as the corresponding phosphates.

Antimony and bismuth give no free acids, though salts of the III and V states are found, and are discussed in the is always six, not four as with phosphorus and arsenic. also known and its structure is shown in Fig. 1 7.3 7d. A phosphorus selenide of composition P 2 Se 5 has been found to have the structure shown in Fig. 17.37e. In marked contrast to phosphorus and arsenic, nitrogen sulfides are rare and a good example is given by the contrast in stabilities between the very stable N 2 0 and the transient sulfur analogue N 2 S which has only been detected spectroscopically. The five elements of the nitrogen Group all give all the trihalides, MX 3 . The least stable are the nitrogen compounds of which only NF 3 is stable and occurs as the expected pyramidal molecule formed by the reaction of nitrogen with excess fluorine in the presence of copper. NF 3 has almost no donor power and has only a very low dipole moment as

TABLE 17.1 3 Oxyacids and oxyanions of the nitrogen Group 467 (a) 9 P • As O S Q Se FIG. 17.3 7 The structures of (a) P 4 S 3 , (b) P 4 S 5 , (c) P 4 S 7 , (d) As 4 S 4 , (e) P 2 Se 5

As a ligand in metal complexes, PF 3 (and to a

lesser extent PCI 3 ) resembles CO, with both

being moderate a donors and good n acceptors.

Thus, for example, Ni(PF 3 ) 4 is similar to

Ni(CO) 4 , cf. Section 16.2.4. QSb O F FIG. 17.3 8 The structure of the ion, Sb 2 F7 the strong N-F bond polarizations practically cancel out the effect of the lone pair. Nitrogen trichloride decomposes explosively. NI 3 is typically prepared as an unstable ammoniate such as NI 3 .6NH 3 , which is highly shock sensitive when freed from excess ammonia. The structure of one ammoniate, NI 3 .NH 3 , has been determined crystallographically. It consists of chains of NI 4 tetrahedra formed by sharing corners and the NH 3 molecules are bonded to the nonbridging iodines. NI 3 free from ammonia has been prepared only recently by the reaction of boron nitride with IF: BN + 3IF -> NI 3 + BF 3 The free NI 3 is rather unstable but can be sublimed as a deep red solid which reacts with ammonia to form the ammoniate NI 3 .3NH 3 . The other sixteen trihalides of the Group are all relatively stable molecules, with the expected trigonal pyramidal structure in the gas phase. The pyramidal structure is also found in many of the solids, but other solid state structures are also found,

particularly among the tri-iodides which adopt layer lattices with the metal atoms octahedrally surrounded by six halogen atoms. PI 3 has three P-I distances of 246 pm (and IPI angles of 102°) and three of 367 pm (angles 60°) showing the P lone pair is still sterically important. In addition to the simple trihalides, MX 3 , a wide variety of mixed halides, MX 2 Y or MXYZ, are found. All the trihalides are readily hydrolysed, giving the oxide, oxyanion, or—in the cases of antimony and bismuth—the oxycation, MO + . They may act as donor molecules, by virtue of the lone pair, and PF 3 in particular has been widely studied. It is rather less reactive to water and more easily handled than the other trihalides. Protonation of PF 3 (but not the lower basicity AsF 3 ) can be achieved with the very strong acid HF/SbF 5 , giving the PF 3 H + ion (CO has a similar low proton affinity). Complex ions, such as SbF 2 ", are formed, and SbF 3 also gives the interesting dimeric ion, Sb 2 F^ (Fig. 17.38). In mixed oxidation state fluorides, such as Sb 8 F 30 , antimony(III) cations are found as well as the [Sb v F 6 ]~ anión. This compound contains [Sb 2 F 5 ] + and [Sb 3 F 7 ] 2+ together with three anions. The cations are linked through single, nearly linear, F bridges, e.g. [F 2 Sb-F-SbF 2 ], and with angles at Sb around 80°. For the heavier halogens, X = Cl, Br or I, three types of complex ion are found: SbXj,SbX5~ and SbX¿~. The first two have the AB 4 L (Fig. 4.4b) and AB 5 L (Fig. 4.5b) structures expected from the presence of the lone pair, but the SbX¿~ species are regular octahedra. In this they parallel the seven-electron-pair MX 2 ," species formed by the heavy elements of the oxygen Group (compare Section 17.7.4). In complex ions of formula M 2 Xg~, a range of structures is found, from the binuclear (Fig. 17.39a; two octahedra sharing a face) through the tetrameric structure of Bi 4 Cl^ to the polymeric [Sb 2 Cl9~] x unit where each antimony carries three terminal Cl atoms, and is linked by three single Cl bridges to three different neighbours in a double-chain. Hydrolysis yields [Sb 2 OCl 6 ] 2 ~ with the triply-bridged structure of Fig. 17.39b. A similar structure is found for [As 2 SBr 6 ] 2 ~ and for [Sb 2 SCl 6] 2~. The trihalides are common reaction intermediates, and, for example, react with silver salts to give products such as P(NCO) 3 , and with organometallic reagents to give O N N O The loosely-bonded N O dimer (a) Sb Br (b) The structure of NO 2 O O The structure of N 2 O 4 N N o/ ∖ The structure of the N 2 O 3 " anión N=N frans-N 2 F 2 c/s-N 2 F 2 The structure of N 2 F 4 Q Sb O CI • O FIG. 17.39 The structures of (a) the M 2 Bnj~ ion, (b) the [Sb 2 OCI 6 ] 2 ~ ion a wide variety of organic derivatives, MR 3 . Among such analogues we note species like As(OTeF 5 ) 3 and

Sb(CF 3 ) 3 where the ligands behave very similarly to F and have a similar extensive chemistry. 17.6.4 Other oxidation states A number of oxidation states other than V and III are found, especially among the oxides and oxyacids. Nitrogen forms the I, II and IV oxides, N 2 0, NO and N0 2 or N 2 0 4 . Nitrous oxide, N 2 0, is formed by heating ammonium nitrate solution or hydroxylamine and is fairly unreactive. It has a 7i-bonded linear structure, NNO. Nitric oxide has already been discussed from the structural point of view. Although it has an unpaired electron, it shows little tendency to dimerize, though some association to rather loose dimers occurs in the liquid and solid. It rapidly reacts with oxygen to form NO 2 . This is also an odd electron molecule but does dimerize readily to dinitrogen tetroxide. The solid is entirely N 2 0 4 and this dissociates slightly in the liquid and increasingly in the gas phase until, at 100°C, the vapour contains 90% NO 2 . NO 2 is brown and paramagnetic and has an angular structure with ONO = 134°. N 2 O 4 is colourless and diamagnetic with a symmetrical structure and a very long N-N bond of 175 pm (compare 145 pm for the N-N single bond length in a molecule like hydrazine). The compound called AngelCs salt, Na 2 N 2 0 3 .H 2 0, is formally N(II). The anión has the structure shown. Here the unique NO distance is 135 pm and the others are 131 to 132 pm. When P 2 0 3 is heated above 210°C a third oxide, P0 2 , is formed, along with red phosphorus. This compound has a vapour density corresponding to PsOia and it behaves chemically as if it contains both P(V) and P(III). It may also contain P-P bonds as it reacts with iodine to give P 2 I 4 . Its structure is unknown. The phosphorus oxide PO, which is isoelectronic to the nitrogen analogue NO, is believed to be the most abundant phosphorus-containing molecule in interstellar clouds. Several metal complexes containing PO as a bridging ligand are known. Heating either Sb 4 0 6 or Sb 2 O 5 in air above 900°C gives an oxide of formula Sb0 2 . This consists of a network of fused Sb0 6 octahedra containing both Sb(III) and Sb(V). A corresponding AsO 2 may exist. There are also two oxyacids of low oxidation states in the Group. These are hyponitrous acid, H 2 N 2 O 2, with nitrogen (I), and hypophosphorous acid, H 3 P0 2, with phosphorus (I). These are included in Table 17.13. Nitrogen forms its low oxidation state in hyponitrous acid by p^-p^ and N-N bonding, while phosphorus in hypophosphorous acid is tetrahedral

(a)

(b)

(c) Q B i O CI

FIG. 17.4 0 The structures of (a) BiCI 2 5  $^{\sim}\!\!,$  (b) Bi 2 Cljj $^{\sim}\!\!$  and

(c) Bi^+ and the low oxidation state arises from two direct P-H bonds. Intermediate phosphorus oxidation states in oxypolyphosphorus compounds resulting from P-P and P-H bonds are shown in Table 17.13 and Fig. 17.36c, d p.467. Lower oxidation state nitrogen fluorides are made by direct combination using less fluorine than required for NF 3 . N 2 F 2 has a planar structure which is most stable in the trans form, but which may also occur in the cis form. There is a n bond between the two N atoms which have each a lone pair. N 2 F 4 is a gas with a skew structure similar to that of hydrazine. In the gas and liquid phases it undergoes reversible dissociation to NF 2 : N 2 F 4 - 2NF 2 similar to that of N 2 0 4 . NF 2 is an angular molecule and contains an unpaired electron. For an odd-electron species, it has fairly high stability resembling NO, NO 2 and C10 2 in this respect. Phosphorus forms X 2 P-PX 2 lower halides of which P 2 I 4 is the most stable. These compounds probably have a skew structure as in N 2 F 4 . The first phosphorus halide with three linked P atoms, P 3 I 5 , has been generated in solution by reaction of PI 3 , PSC1 3 and Zn, and found by nmr spectroscopy to have the structure I 2 P-P(I)-PI 2 . The lower halides of bismuth present a much more complicated picture. When bismuth is dissolved in molten bismuth trichloride, an intensely coloured solution results from which may be isolated a compound with the accurate formula Bi 12 Cl 14 . This is a complicated structure with 48 Bi atoms and 56 Cl atoms in the unit cell. These are arranged as 4Bic + , SBiClg" and 2Bi 2 Cl8~ units. The BiCl^" ion is a square pyramid with Bi(III) and resembles the SbF^" ion mentioned earlier. In the structure these units are weakly linked to each other to form a chain. The Bi 2 ClQ~ unit contains Bi(III) and consists of two square pyramids sharing an edge of the base with their apices trans to each other. The Big + unit has six Bi atoms at the corners of a somewhat distorted trigonal prism, and the other three Bi atoms above the rectangular faces. These units are shown in Fig. 17.40. Thus the solid may be written (BÍ9 + ) 2 (BiCl5~) 4 Bi 2 Clg~. In Bi 10 Hf 3 Cl 18 , the Bi + ion has been recognized along with Big + and HfCl¿~ ions. Further work has produced other cluster compounds of Bi and Sb, and these are reviewed in Section 18.4. In Bil, an infinite chain structure is found, where Bi atoms are in two environments (Fig. 17.41). In the A chain, Bi is bonded only to three other Bi atoms, and is formally Bi(0). In the B chain, there are four Bi-I bonds, each shared with a second Bi, and thus with the formal oxidation state Bi(II). These Bi atoms form a fifth bond to a bismuth of the A chain. O Bi O ' FlG. 17.41 The structure of Bil In the lower bromides we find BiBr, isostructural with Bil, and also Bi 12 Br 14 , comparable with Bi 12 Cli 4 . Negative oxidation states appear in the hydrides, MH 3 , and in the organic compounds, NR 3 . The other elements, except possibly arsenic (see Table 2.14), are of lower electronegativity than carbon in alkyl groups, and their organic compounds correspond to positive oxidation states. This distinction is not a useful one and is best regarded—as in the case of carbon chemistry in general—as an accidental result of the definitions. The organic compounds, MR 3 , and organohydrides such as R 2 PH, behave in a similar way to the hydrides B A B but with the M-C bond stronger than M-H. An extensive organometallic chemistry of this Group exists which requires a textbook of its own for review. Here we note only some direct comparisons with the hydrides. As well as MR 3 , analogous to MH 3 , ions NRj, PRj, AsRj, SbRj and BiR^ exist which are tetrahedral and analogous to NH|. The phosphorus analogue of NHj exists, for example in PH 4 I which is prepared from PH 3 and HI. However, the phosphonium halides are relatively unstable and readily decompose to phosphane and hydrogen halide. They are much more covalent than the ammonium salts. The analogous AsHj and SbHj ions have also been recently prepared as their SbF^ salts by protonation of the parent hydride MH 3 using the superacid HF/SbF 5 . Although no pentavalent hydride, MH 5 , exists, the pentaphenyl phosphoranes MPh 5 of P, As, Sb and Bi exist, as does PMe 5 .PPh 5 and AsPh 5 are trigonal bipyramids in shape but SbPh 5 is a square pyramid. SbPh 5 reacts with PhLi to give the octahedral SbPh^ ion. BiMe^ is also known and has the expected octahedral geometry. A number of mixed chloro-alkyl or chloro-aryl phosphoranes, R n PX 5 \_ n (R = alkyl, aryl; X = halide), are also known, comparable with PH 2 F 3 and similar hydride-halides. As a result of recent studies the chemistry of these species has been found to be more complex than first thought. Species of this type can occur in a variety of forms and as a general illustration we take Ph 3 PI 2 . Reaction of Ph 3 P with di-iodine in ether gives the molecular four-coordinate compound Ph 3 P-I-I and neither ionic [Ph 3 P-I + ]r or 5-coordinate covalent phosphorane Ph 3 P(I)(I) which were previously thought to be the stable forms of this compound. Ph 3 P-I-I can be thought of as a donor-acceptor compound between Ph 3 P and I 2 . Analogous compounds Ph 3 P-Br-Br and Ph 3 As-I-I can also be formed. There appears to be a delicate balance of factors determining whether a covalent

or ionic form is produced since PhPCl 4 is a molecular compound whilst the corresponding methyl analogue exists as [MePCl 3 ] + Cr. In addition, when R 3 P-I-I compounds are dissolved in chloroform they ionize to [R 3 P-I] + r. Nitrogen is found in the -II state in hydrazine and its organic derivatives, R4N 2 , and in the -I state in hydroxylamine, NH 2 OH. 17.7 The oxygen Group, ns 2 np 4 17.7.1 General properties Table 17.14 lists some of the properties of the elements and Fig. 17.42 and 17.43 show the variations with Group position of a number of parameters and of the oxidation state free energies: Oxygen occurs both as the O 2 molecule and as ozone, 0 3 . 0 2 is paramagnetic (Section 3.5) and has a dissociation energy of 489 kj moP 1 It is pale blue in the liquid and solid states. Ozone is usually formed by the action of an electric discharge on 0 2 , but it can also be formed chemically by the reaction of Oj (dioxygenyl, Section 17.7.2) salts with water in HF at low temperature. Pure 0 3 is deep blue as the liquid with m.p. = -250°C and b.p. = -112°C. It is diamagnetic and explodes readily as the decomposition to oxygen is exothermic and easily catalysed: 03=802, A#=-142 kJmoP 1

elements will be found in the following places: Polysulfides and polyselenides are discussed in fuller detail in Section 18.2 and metal-polysulfur com

lonization potentials Table 2.8 pounds are covered in Section 19.2. Metal dioxygen

Atomic properties and electron species are covered in Section 16.9 with structural

configurations Table 2.5 parameters in Table 16.5.

Radii Table 2.10, 2.11, 2.12

Electronegativities Table 2.14

Redox potentials Table 6.3 471

TABLE 17.14 Properties of the elements of the oxygen Group Element Oxygen Sulfur Selenium Tellurium Polonium Symbol 0 S Se Te Pô Oxidation states -II, H) -II, (II), IV, VI (-11), (II), IV, VI II, IV II, IV Coordination numbers 1, 2, (3), (4) 2 , 4 , 6 2, 4, 6 6 Availability Common Common Common Common Very rare

Ozone occurs in the upper atmosphere, where it

is formed photochemically from 0 2 , and has the important property of absorbing harmful middle and far-UV radiation. The recent 'hole' in the ozone layer, caused by chlorofluorocarbons and related materials, is of significant current con cern and this topic is discussed in greater detail

in Chapter 20. Ozone has an angular structure with the OOO angle equal to 117°. The bonding in ozone has been described briefly previously in Section 4.10. Of the eighteen valency electrons, four are held in the a bonds and eight in lone pairs on the two terminal oxygens. Two are present as a lone pair on the centre oxygen, leaving four electrons and the three p orbitals perpendicular to the plane of the molecule to form a n system. The three p orbitals combine to form a bonding, a nonbonding and an antibonding three-centred n orbital and the four electrons occupy the first two. There is thus one bonding n orbital over the three 0 atoms giving, together with the a bonds, a bond order of about one and a half. The bond length is 128 pm which agrees with this; 0-0 for a single bond in H 2 0 2 is 149 pm while 0=0 in 0 2 is 121 pm. Adding one more electron to form the 0^~ ion starts to populate the antibonding n\* orbital, and we find the bond length increases to 133 pm with an angle of 114°. Ozone is a strong oxidizing agent, especially in acid solution where the potential is 2.07 V (Table 6.3). It is exceeded in oxidizing power only by fluorine, oxygen difluoride and some radicals. Since the S-S single bond is strong, sulfur chains form readily, and polysulfur species are one of the major classes of catenated compounds. The S-S bond is also labile, so that a particular chain compound, such as S 6 C1 2 , readily redistributes into an equilibrium mixture of different chain lengths, leading to difficulties in characterizing such compounds. The element sulfur itself occurs as chains or rings (which are simply closed chains), and its structural complexities are now understood. Sulfur shares with phosphorus the ability to form a wide variety of allotropie forms in all three phases. However, many of these varieties of sulfur turn out to be mixtures of long chains and rings. The main interrelations are shown in Fig. 17.44. Under normal conditions, the thermodynamically stable form of sulfur is the S 8 ring which has the crown structure shown in Fig. 17.45. If we consider a short chain of S atoms .2 I o o. §> ï∗ c o i ÏÉ Se Te s 250 ∖& 150 | 5

0 ! 0 .. A-- A-' Se Te FIG. 17.42 Some properties of the oxygen Group elements. The radii of the anions, X 2 , are almost identical with the corresponding Van der Waals' radii 6.0 5.0 4.0 E 3.0 ^ 2. 0 ¿ 1. 0 ^ 0. 0 -1.0 -2.0 -3.0 -II I 0 I I I II I oxidation stat e •AS IV V VI FIG. 17.43 Oxidation state free energies of the oxygen Group elements. Oxygen shows only negative oxidation states. The -II state becomes decreasingly stable from 0 to Po. The positive oxidation states show the drop in stability of the VI state after S and the tendency for intermediate states to be the more stable for Se and Te. Polonium values are not known GAS b.p. 444.6°C >(S 6 ) T increase S 8 rings LIQUID monoclinic rhombic m.p.119°C m.p.112.8°C S n chains I rapid cooling plastic (S n chains) P decrease rapjdcoo|ing to-196°C | purple, paramagnetic solid (S 2 molecules ) >-80°C «tanHinn Slow , 95.5°C SOLID Engel' s sulfurf!?^ rhombic \_ ' (S 6 rings) (S 8 rings) monoclinic (S 8 rings) Na 2 S 2 O 3 + cone. HCI FIG. 17.44 The interconversion of the allotropes of sulfur FIG. 17.45 The structure of the S 8 or Se 8 ring (say S-S-S-S), then the central S forms two bonds and has two lone pairs. The SSS angle is thus expected to be around 105° and the chain is a zigzag. Further, the arrangement will twist to move lone pairs as far apart as possible, so we find an optimum dihedral angle (angle between successive SSS planes), which minimizes lone pair repulsions, of around 85-100°. Putting these preferred angles together, we find that a long chain of S atoms will tend to coil up and 'bite back' on itself. With an arrangement of 8 S atoms, the resulting ring allows an optimum choice of angles. Several of the allotropes (more specifically polymorphs) of sulfur contain the S 8 ring and differ in the ways in which the rings are packed in the solid. When sulfur is heated to about 160°C, there is a sudden large increase in viscosity and this is ascribed to the Sa-^S^ change from rings to long chains of S atoms. The S 8 ring is also found in the gas phase, together with smaller units. A second, long-known, orange-red form of sulfur was first reported by Engel. It has S 0 rings, arranged in the chair form. This, and the many more recently discovered sulfur rings, is treated in Section 18.2. A further interesting modification of sulfur is the S 2 unit which occurs in the gas at high temperatures. On rapid cooling it condenses to a purple solid, which is paramagnetic like the isoelectronic 0 2 . 7 Se <Te 473

All polonium isotopes have relatively short half

lives and this isotope, polonium 210, is the

longest-lived with fi = 138 days. The isotopes

all have high activity and the handling problems

are severe so that polonium chemistry is not

fully explored.

Dioxygen coordinates to a variety of transition

metals in species which have been variously

formulated as containing neutral 0 2 , superoxide

C>2 or peroxide O∖~. These are discussed in

Section 16.9. Selenium also forms a number of allotropes. Two different red forms containing Se 8 rings are found but the stable modification is the grey form. This contains infinite spiral chains of selenium atoms with a weak, metallic interaction between atoms in adjoining chains. The chain form of sulfur also contains spiral chains but has no metallic character. Tellurium has only one form in the solid. This is silvery-white, semi-metallic, and isomorphous with grey selenium, but with rather more metallic interaction as the selfconductivity is higher. In the vapour, selenium and tellurium have a greater tendency than sulfur to exist as diatomic and monatomic species. Polonium is a true metal with two allotropie forms, in both of which the coordination number is six. Polonium is found in small amounts in thorium and uranium minerals (where it was discovered by Marie Curie) as one of the decay products of the parent elements, Th or U. It can now be more readily made by bombarding bismuth in a reactor: 2 «Bi + Jn^3Bi^7 4 Po + > The trends observed in the nitrogen Group appear in a more marked degree in the chemistry of the oxygen Group. The -II state is well established, not only for oxygen, but also for sulfur and even selenium, and it often occurs as the M 2  $^{\sim}$  ion in the compounds of these elements. Apart from the Group state of VI, both the IV and the II states are observed in the Group, the IV state becoming the most stable one for tellurium, and the IV or II state the most stable one for polonium. Apart from the fluorine compounds, oxygen appears only in the -II state, except for the -I state in the peroxides. A variety of shapes is again observed. The VI state is usually octahedral or tetrahedral while the presence of the nonbonding pair in compounds of the IV state gives distorted tetrahedral shapes in the halides, MX 4 , and pyramidal or V shapes in oxyhalides or oxides. Coordination numbers higher than six are uncommon

but TeF 6 does add F~ to give TeF^~. Oxygen has little in common with the other elements in the Group apart from formal resemblances in the -II states. Polonium shows signs of a distinctive chemistry, similar to that of lead or bismuth, but the difficulties of studying the element mean that there are many gaps in its known chemistry. Tellurium resembles antimony in showing a strong tendency to be 6-coordinate to oxygen, while sulfur and selenium show 4-coordination. Sulfur is stable in the VI state, while selenium (VI) is mildly oxidizing. The tendency to catenation shown by the elements is continued in the compounds, especially those of sulfur. Oxygen forms O-O links in the peroxides and in 0 2 F 2 , and threeand four-membered chains may be present in the unstable fluorides, 0 3 F 2 and 0 4 F 2 . Sulfur forms many chain compounds, particularly the dichlorosulfanes, S^C1 2 , where x may be as high as 100, and the polythionates, (0 3 SS^S0 3 ) 2 " where the compounds withx= 1 to 12 have been isolated. Chain-forming tendencies are slight for selenium and absent in tellurium chemistry. It is convenient to discuss oxygen chemistry separately from that of the other elements. 17.7.2 Oxygen Oxygen combines with all elements except the lighter rare gases, and most of the oxides are listed in Tables 13.3 and 17.2. Their properties have been discussed already. The change in acidity from the s element oxides to the oxides of the light p elements will already be familiar to the reader. Oxygen shares with the other first row elements the ability to form p^-p^ bonds to itself and to the other first row elements, and it is sufficiently reactive and electronegative to form p^-d^ bonds with the heavier elements. As fluorine is more electronegative than oxygen, compounds of the two are oxygen fluorides and are discussed here. The halogen oxides of Cl, Br and I are to be found in Section 17.8. Four oxygen fluorides are well established—OF 2 , 0 2 F 2 , 0 3 F 2 and 0 4 F 2 —and two more have been reported relatively recently—0 5 F 2 and 0 6 F 2 . In all of these compounds oxygen is in a formally positive oxidation state and these are the only compounds where this occurs. OF 2 is formed by the action of fluorine on dilute sodium hydroxide solution, while the other five result from the reaction of an electric discharge on an 0 2 /F 2 mixture. An increasing proportion of 0 2 and decreasing temperature are required to make the highest members of the series. Thus 0 5 F 2 and 0 6 F 2 were prepared in

## OXYGEN AND ITS USES

Oxygen is prepared on a large scale by fractionation of used directly in various large-scale organic syntheses liquid air, and had its first large-scale use in the such as the formation of ethylene oxide or propylene

Bessemer steel-making process where it is used to oxide from the alkenes. Smaller-scale uses, often via

reduce the carbon content of iron. It has become more peroxides, are in bleaching, biological and medical

widely used in metallurgy to assist the combustion of work, and sewage treatment,

heavy fuel oils, allowing replacement of coke. It is also a discharge at -213°C using a 5/1 mixture of 0 2 and F 2 . The use of higher proportions of oxygen does not give 0 7 or higher species at this temperature but it might be possible to make these by working at a still lower temperature. All six compounds are very volatile with boiling points well below room temperature. OF 2 is the most stable of the six oxygen fluorides. It does not react with H 2 , CH 4 or CO on mixing, although such mixtures react explosively on sparking. Mixtures of OF 2 and halogens explode at room temperature. OF 2 reacts slowly with water: OF 2 + H 2 0-\*0 2 + 2HF and is readily hydrolysed by base: OF 2 + 20R- -> 0 2 + 2F- + H 2 0 The structure of OF 2 is V-shaped, like H 2 0, with the FOF angle = 103.2° and the bond length, 0-F = 141.8 pm. The other five oxygen fluorides are much less stable. 0 2 F 2 decomposes at its boiling point of -57°C, 0 3 F 2 at -157°C, O 4 F 2 at -170°C, and O 5 F 2 and O 6 F 2 are stable only to -200°C. Indeed, 0 6 F 2 can explode if it is warmed rapidly up to -1 85°C. All are red or redbrown in colour. Electron spin resonance studies on 0 2 F 2 and 0 3 F 2 have shown that these contain the OF radical to the extent of 0.1% for 0 2 F 2 and 5% for 0 3 F 2 . It is likely that the higher members also contain free radicals, and these may account for the colour. 0 2 F 2 has a skew structure similar to that of hydrogen peroxide and the others may be chains, FO^F. When O 2 F 2 is reacted at low temperatures with molecules which will accept F~, such as BF 3 or PF 5 , oxygenyl compounds result: 0 2 F 2 + BF 3 -> (0 2 )BF 4 +£F 2 (at - 126°C) Oxygenyl tetrafluoroborate decomposes at room temperature to BF 3 , 0 2 and fluorine. The oxygenyl group may be replaced by the nitronium ion, NOj : O 2 BF 4 + NO 2 -> (NO 2 )BF 4 + O 2 The oxygenyl ion may also be formed directly from gaseous oxygen by reaction with the strongly oxidizing platinum hexafluoride molecule: 0 2 + PtF 6 -^(0 2 ) + (PtF 6 )Other Oj (MF 6 )~ species have M = P, As, Sb, Bi,

Nb, Ru, Rh, Pd or Au (note the unusual Au(V) state). Oj(M 2 Fn)∼ for M = Sb, Bi, Nb and Ta are also known. Recently Oi (GeF 5 )~ was reported. In all these species the 0-0 stretching lies in the range 1825-1865 cm" 1 , reflecting a stronger bond than in 0 2 . Oxygen forms two compounds with hydrogen, water and hydrogen peroxide, H 2 O 2 . Water, and its solvent properties, is discussed in Chapter 6 and hydrogen-bonding in 0-H systems is included in Section 9.7 and Figs. 9.1 and 9.2. Pure H 2 0 2 is a pale blue liquid, m.p. -0.89°C, b.p. 150.2°C, with a high dielectric constant and is similar to water in its properties as an ionizing solvent. It is, however, a strong oxidizing agent and readily decomposes in the presence of catalytic amounts of heavy metal ions: H 2 0 2 ^H 2 0 +±0 2 Accordingly, stabilizers, such as EDTA, which are good complexing agents for these metal ions, need to be added to prevent catalytic decomposition. Hydrogen peroxide has the skew structure shown in Fig. 9.7b. Finally, it must be noted that the terms, peracid (better, peroxoacid) and peroxide, are properly applied only to compounds which contain the -0-0group, which may be regarded

THE PREPARATION OF HYDROGEN PEROXIDE

Hydrogen peroxide may be prepared by acidifying an

ionic peroxide solution (Section 10.2) or, on a large

scale, by electrolytic oxidation of a sulfate system: 2HSÜ4 -> S 2 Og~ + 2H + + 2e~ S 2 0^ + 2H 3 0 + -> 2H 2 SO 4 + H 2 0 2

(The intermediate is called persulfate.) However, most

hydrogen peroxide today is manufactured by the

anthraquinone autoxidation process. In this a func

tionalized anthraquinone dissolved in an organic

solvent is first reduced (using hydrogen and a catalyst,

typically palladium) to give the corresponding hydro

quinone which is then oxidized using air, giving

hydrogen peroxide and regenerating the anthraqui

none, shown in Fig. 17.46. The hydrogen peroxide is extracted with water in a counter-current process and may

be concentrated by fractionation. Pd catalyst H 2 0 2 FIG. 17.46 The reactions used in the industrial manufacture of H 2 0 2 by the anthraquinone process

#### PEROXOACIDS AND DERIVATIVES

There are a number of covalent peroxy species, acids or oxyanions, which may be regarded as derived from the normal oxygen compounds by replacing -O- by -O-O-; just as H-O-H is related to H-O-O-H. The best known examples are permonosulfuric acid (Caro's acid) H 2 SO 5 —which occurs as an intermediate in the persulfate oxidation above—perdisulfuric acid (per sulfuric) H 2 S 2 O 8 , perphosphoric acid, H 3 PO 5 , and perdicarbonic acid, H 2 C 2 O 6 . The structures of the sulfuric acids have been definitely established and are related to the oxygen compounds as shown in Fig. 17.47. An X-ray structure determination has recently been carried out on explosive crystals of Caro's acid, confirming the expected tetrahedral geometry about sulfur and the presence of an S-O-O-H linkage. The molecules are linked by hydrogen bonding involving both the OH and the OOH groups—S=O- • -HOS and S = O---HOOS. The O-O bond length is 146.4pm, compared with 145.8 pm in H 2 O 2 . The other acids are probably (HO) 2 (HOO)P=O and HO 2 C-O-O-CO 2 H, and the latter has been structurally characterized by an Xray study as its cyclohexyl ester, CyO 2 C-O-O-CO 2 Cy.

is similar to that of peroxydisulfate but with the two PO 3 units lying trans across the planar P-O-O-P link.

The structure of the peroxydiphosphate ion, [P 2 O 8 ] 4 ~,

The overall structure is C 2h . The O-O length is 149 pm. (a)  $\hat{1} > H$  (c)  $\hat{1}$  OOH FIG. 17.47 The structures of the sulfuric and per-sulfuric acids: (a) sulfuric acid, (b) pyrosulfuric acid, (c) peroxymonosulfuric acid, (d) peroxydisulfuric acid ^R OH ,R OH

476 A number of other compounds are commonly termed peroxoacids (or salts thereof) but most are only simple acids with hydrogen peroxide of crystallization. For example, the commercial 'percarbonate' is, in fact,

Na 2 CO 3 .1.5H 2 O 2 . While free percarbonic acid, H 2 CO 4 , is

unknown, the monopotassium salt K[H(O 2 )CO 2 ].H 2 O 2

does contain the peroxocarbonate anión (plus a hydro

gen peroxide of crystallization), where the OH group of

hydrogen carbonate has been replaced by an OOH

group. The peroxocarbonate ion is also known to exist

in transition metal complexes such as: Ph 3 P x Ph 3 P Pt Sodium perborate has also been established as a true peroxy compound with B-O-O linkages, see Section 17.4.1.

Ionic peroxides are discussed in Chapter 10 and

transition metal peroxy compounds in Chapter

16. as derived from hydrogen peroxide. In the older literature, and in much technical literature, some higher oxides such as Mn0 2 are termed peroxides. This usage is incorrect on the modern convention of nomenclature. 17.7.3 The other elements: the VI state The trioxides, M0 3 , of the VI state are formed by sulfur, selenium, tellurium and polonium, and all these elements (except possibly^polonium) form oxyanioas. The acids are included in Table 17.15. Sulfur and selenium are 4-coordinated to oxygen in the acid H 2 M0 4 and in the anión (M0 4 ) 2 ~. In the Na 2 SeO 4 ∕Na 2 0 reaction system, new selenium oxyanions SeOa∼ (with Se0 4  $^{\sim}$  in Na 6 Se 2 0 9 ) and SeOs" (in Na 4 SeO 5 ) have been obtained. Tellurium forms the dibasic, 6-coordinated acid Te(OH) 6 , and two series of 6-coordinated tellurates, TeO(OH)5 and TeO 2 (OH)íi~. In addition, the compound Rb ó (Te 2 0 9 ) has been shown to contain equal numbers of tetrahedral [Te0 4 ] 2 ~ and trigonal bipyramidal [Te0 5 ] 4 ~ ions. Sulfur, selenium and tellurium all bum in air to form the dioxide, M0 2 , and the trioxides are made by oxidizing these. Sulfuric acid, H 2 S0 4 , is formed by dissolving S0 3 in water, but selenic acid, H 2 Se0 4 , is more readily made by oxidizing the selenium(IV) acid, H 2 Se0 3 , made by dissolving Se0 2 . Sulfuric acid and the sulfates are stable, while selenic acid, the selenates, telluric acid and the tellurates are all oxidizing agents, although they are typically slow in reacting. Only sulfur gives a condensed acid in the VI state, and it forms only the binuclear species, pyrosulfuric acid H 2 S 2 O 7 . Condensed anions include S 3 O 2 o and S 5 O^ as well as M 2 0y∼ (M = S, Se), but tellurium gives no polyanions at all. As condensation is also restricted in the IV state to binuclear compounds of sulfur and selenium, it will be seen that the tendency to condense is much slighter in this Group than it was in the nitrogen Group. Oxidizing power of the VI state increases down the Group, and polonium(VI) is strongly oxidizing, so that the existence of the oxide and oxyanions is in some doubt.

OCCURRENCE AND USES OF \$, se AND Te

Sulfur occurs as the free element, especially in volcanic areas around hot springs, and was one of the elements known in ancient times. Its main current source is from the desulfurization of oils and natural gas, mining in volcanic deposits, as a byproduct of extracting sulfide ores, and by the Frasch process where it is recovered from under ground deposits by hot water under pressure. Its major use is in sulfuric acid manufacture, with minor consumption in many industries, especially rubber manufacture. Sulfuric acid is made by burning S to SO 2 , followed by catalytic oxidation to SO 3 and solution in sulfuric acid and dilution. More than half the sulfuric acid is used in fertilizer manufacture, with other uses spread over more than a hundred industries. Selenium and tellurium are byproducts of copper extraction. Selenium is used in glass, as a decolorizer and to produce red and yellow colours. It is used in photoconductors and electronic devices, and is the photoreceptor which is basic to xerographic photocopying. Tellurium finds uses in metallurgy and alloys. CHAPTER 17 477 (a) (b) (c ) (d ) FIG. 17.4 8 Oxyhalides of sulfur; (a) SO 2 X 2 , (b) S 2 0 5 F 2 (or CI 2 ), (c) SOF 4 , (d) SOF 61 (e) SO 3 F 2 •^-•OF V (e) (a) (b) Te' (c)

FIG. 17.4 9 (a) F 2 Te(OTeF 5 ) 4 , (b) (F 5 Te) 2 0, (c) (F 4 Te) 2 (0) 2 The other main representatives of the VI state are the hexafluorides, MF 6 . These compounds are all relatively stable but with reactivity increasing from sulfur to tellurium. SF 6 is extremely stable and inert, both thermally and chemically, and is used as an inert dielectric medium in a number of electrical devices. However, in the presence of oxygen an electrical discharge can generate species such as F 5 S-0-SF 5 and the peroxy analogue F 5 S-00-SF 5 . SeF 6 is more reactive and TeF 6 is completely hydrolysed after 24 hours contact with water. The hexafluorides are more stable, and much less reactive as fluorinating agents, than the tetrafluorides of these elements. All the hexafluorides result from the direct reaction of the elements, and dimeric molecules S 2 Fi 0 or Se 2 F 10 are also found (but not Te 2 F 10 ). These compounds are rather more reactive than the hexafluorides, but still reasonably stable. The coordination is octahedral, F 5 M-MF 5 . They hydrolyse readily, with fission of the M-M bond, and S 2 F 10 reacts with chlorine to give the mixed hexahalide, SF 5 C1. Addition of GIF to SeF 4 gives SeF 5 Cl and tellurium forms similar species, TeF 5 X for X = Cl, OF or OCL Pseudohalide compounds such as SF 5 CN are also known. Tracer studies reveal the existence of a volatile polonium fluoride, probably PoF 6 . TeF 6 adds F~ to form an 8-coordinated anión and also reacts with other Lewis bases, such as amines, to give 8-coordinated adducts like (Me 3 N) 2 TeF 6 . The VI state is also found in sulfur and selenium oxyhalides, and in halosulfonic acids. Sulfur gives sulfuryl halides, S0 2 X 2 , with fluorine and chlorine, and also mixed compounds S0 2 FC1 and S0 2 FBr. Only one selenium analogue, Se0 2 F 2 , is found. If one OH group in sulfuric acid (Fig. 17.47a) is replaced by F, fluorosulfonic acid results. The anión has

been characterized and shows the expected tetrahedral configuration around S with the S-F bond distance of 165 pm and the other three S-0 distances equal to 143 pm: the SOF bond angle is 108°. Sulfur also gives a number of more complex oxyhalides, some of which are shown in Fig. 17.48. The oxyhalides are formed from halogen and dioxide, or from the halosulfonates. S0 2 F 2 is inert chemically but the other compounds are much more reactive and hydrolyse readily. Tellurium, in particular, forms a number of oxyfluorides of complex formula such as Te 5 O 4 F 22 or Te 7 O 0 F 3 o. Structural studies show that many of these are derived from TeF 6 by successive replacement of F by the OTeF 5 group. There is evidence for F 4 Te(OTeF 5 ) 2 , F 2 Te(OTeF 5 ) 4 , FTe(OTeF 5 ) 5 and Te(OTeF 5 ) 6 (e.g. Fig. 17.49a). The structures are octahedral, and cis and trans isomers of both the F 4 Te0 2 and F 2 Te0 4 species are known. Related species are (TeF 5 ) 2 0 and (TeOF 4 ) 2 which is a pair of octahedra linked by two oxygen bridges (Fig. 17.49b, c). The selenium analogue is also found. (These structures contrast with the transition metal analogues, such as WOF 4 , which are linked by fluorine bridges.) The OTeF 5 and OSeF 5 groups are found to bond to other atoms. Thus we find V(OTeF 5 ) 6 with an octahedral V0 6 configuration. Similar species include I(OSeF 5 ) 5 , B(OTeF 5 ) 3 and Xe(OTeF 5 ) /? for n = 2, 4 and 6. There is a range of angles at 0 from XeOTe (125°), TeOTe (139°) to VOTe (170°) which suggests an increasing degree of M-O-Te n bonding. The simple species F 5 MOMF 5 is found for M = S, Se and Te, each with similar MOM angles of 142-5<sup>°</sup>, and in each case the fluorines are eclipsed, again arguing for a p^-d^ interaction of the oxygen lone pairs. As this field develops, it is becoming apparent that the OSeF 5 and OTeF 5 groups are behaving very like F, as ligands of high electronegativity. Many species occur in which O P O F F O

(a)

- (f)
- (g) ' \
- (h) Q s Be O O

FIG. 17.50 Oxygen compounds of sulfur and selenium: (a)

S0 2 , (b) Se0 2 , (c) S(or Se)0r (sulfite, selenite), (d) S 2 0?"

(pyrosulfate), (e) S 2 06~ (dithionate), (f) S 2 0^

#### (pyrosulfite),

(g) S 3 0jj- (trithionate), (h) S 4 0i $^{\sim}$  (tetrathionate; related

SflO^ have different numbers of sulfur atoms in a chain

between the two terminal S0s~ groups) stepwise replacement of F is found, as above and also in oxyfluorides like OXe(OTeF 5 ) 4 (cf. OXeF 4 ), as ionic species, e.g. Na + (OSeF 5 )~, and halo-species as ClW(OTeF 5 ) 5 . Three halosulfonic acids are known, FS0 3 H, C1S0 3 H, and BrSO 3 H. The structures are tetrahedral and are formed from sulfuric acid by replacing an OH group by a halogen atom. They are strong monobasic acids but only fluorosulfonic acid is stable and forms stable salts, fluorosulfonates FSCÇ, which are similar in structure and solubilities to the perchlorates. Hexavalent aryl tellurium compounds are also known, such as Ph 6 Te, Ph 5 TeCl and Ph 5 Te + . The latter has a square pyramidal geometry, analogous to the structure of the isoelectronic Ph 5 Sb. 17.7.4 The IV state The IV state is represented by oxides, M0 2 , halides, MX 4 , oxyhalides, MOX 2 , acids and anions, for all four elements. Sulfur(IV) is reducing, selenium(IV) is mildly reducing (going to Se(VI)) and also weakly oxidizing (going to the element), tellurium(IV) is the most stable state of tellurium, while polonium (IV) is weakly oxidizing (going to Po(II)). In addition, a number of complexes are known. The oxides are given in Table 17.2a and the acids and anions in Table 17.15. The dioxides result from direct reaction of the elements. S0 2 and Se0 2 dissolve in water to give the acids, but Te0 2 and Po0 2 are insoluble and the parent acids do not exist. Tellurium and selenium oxyanions result from the solution of the oxides in bases. Salts of one condensed acid exist: these are the pyrosulfltes, \$205", which have the unsymmetrical structure with a S-S bond, ~0 3 SSO^. Figure 17.50 gives the structures of some of the oxides and oxyions. The IV state oxides and oxyanions have an unshared electron pair (in monomeric structures) and thus have unsymmetrical structures. The stable form of the dioxide shows an interesting transition from monomeric covalent molecule, S0 2 , through polymeric covalent, Se0 2 , to ionic forms for Te0 2 and Po0 2 . Sulfur, selenium and tellurium dioxides are acidic and dissolve in bases. Po0 2 appears to be more basic than acidic and dissolves in acids as well as forming polonites with strong bases. One compound intermediate between the IV and VI oxides is reported. This is Se 2 0 5 , formed by controlled heating of Se0 3 . This compound is conducting in the fused state and it has been suggested

that it is Se0 2+ Se0 4 ~, a salt of Se(IV) and Se(VI). The known tetrahalides are listed in Table 17.2b. The missing ones are SBr 4 , SI 4 and SeI 4 while SC1 4 and SeBr 4 are also unstable, SC1 4 decomposing at —3°C. The tellurium tetrahalides are markedly more stable, even TeI 4 being stable up to 100°C. TeCl 4 , TeBr 4 and SeCl 4 are all stable up to 200°C and the tellurium compounds to 400°C. All the tetrafluorides are known and these are rather more stable than the other tetrahalides to thermal decomposition. They are much more reactive than the hexafluorides and act as strong, though selective, fluorinating agents. All four polonium tetrahalides are known and resemble the tellurium analogues, though they seem to be rather less stable. The structures of most tetrahalides are known. SF 4 , SeF 4 , TeBr 4 and TeCl 4 , are all found as the distorted tetrahedron derived from the trigonal bipyramid with one equatorial position occupied by an unshared pair of electrons (see Section 4.2). Tellurium tetrafluoride forms a polymeric structure in which square pyramids are linked into chains by sharing corners, TeF 3 (F 2/2 ). TeI 4 is a tetramer consisting of four TeI 6 octahedra sharing edges. Thus the lone pair is still sterically active. SC1 4 and SeCl 4 exist only in the solid and vaporize as MC1 2 + C1 2 - the sulfur compound at -30°C and the selenium one at 196°C. Raman spectra suggest the solid is MClJ CP and this is supported by crystallographic evidence for EBrJ and Elj (E = S, Se) in addition to more complex cations like Se 2 I 4 + . The selenium and tellurium, and probably the polonium, tetrahalides readily add one or two halide ions to give complex anions such as SeF5~ and MXÍ~ (M = Se, Te, Pô; X = any halogen). These hexahalo(IV) complex ions are interesting from the structural point of view as they contain seven electron pairs. Structural determinations on a number of compounds show that the MXÍ''' group is octahedral, but the group may be regular or distorted. The electron pair repulsion theory, discussed in Chapter 4, would imply that the nonbonded pair occupied a spatial position and should lead to a distorted octahedron. It is possible,

- (b)
- (c)
- (d)
- (e)

\$Q 2 AS A LIGAND

Sulfur dioxide is a very versatile ligand, able to coordinate to metal centres in many different ways, either through oxygen or sulfur atoms, n bonded, or as a bridging ligand either through sulfur, or sulfur and oxygen. It is also chemically reactive, and can act either as an oxidant, reductant, or small reactive molecule which can undergo insertion reactions e.g. into metal carbon bonds. As an example of a homoleptic S0 2 complex, containing only SÛ2 ligands, oxidation of Ni with AsF 5 in liquid S0 2 gives [Ni(S0 2 ) 6 ] 2+ , with 6 0-bonded S0 2 ligands arranged octahedrally around the metal centre. LíQ ^s I S^ I? M N o o S-bonded 0-bonde d rc-bonde d bridging

Reference

G.J. KUBAS, Accounts of Chemical Research

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FiG. 17.5 1 The structure of thionyl halides, SOX 2 \ 9 ATr ' ¿ v° cA Stucture of the [Te 3 0 6 F 3 ] 3 ~ ion however, that with large, heavy, central atoms, the nonbonded pair might be accommodated in an inner orbital rather than in a particular spatial direction. Structural studies so far reported indicate that two groups of structures are found. In the hexafluorides of the IV state, MFo", as in the isoelectronic IF¿~ and XeF 6 , the structure is distorted octahedral, indicating a sterically active lone pair. However, in the heavier halides like MClo™~, the structure is regular octahedral. It is proposed here that the dominant factor is repulsion between halogen atoms which is minimized in the regular structure. In this form, the lone pair would have to occupy an s orbital presumably. The structures of pentafluoro anions, [EF 5 ]~ for E — S, Se, Te and various cations, are all square pyramids with the lone pair to complete the octahedron. The TeF^ units link into chains by weak Te-F- • -Te bonding while the Se analogue shows weakly bonded tetramers. As in TeF 4 , the E atoms lie below the base of the square pyramid, that is, the base F atoms are bent up away from the lone pair position. It will be recalled from Section 13.6 that the opposite distortion occurs when there are five ligands and no lone pair. Selenium forms an interesting pair of dinuclear complexes in the IV state. Se 2 Cli^ has two octahedra sharing an edge, while Se 2 CC has two octahedra sharing a face (alternatively seen as two Se atoms linked respectively by 2 or 3 bridging Cl). Oxyhalides of the IV state are formed only by sulfur and selenium and have the formula MOX 2 . Thionyl halides, SOF 2 , SOC1 2 , SOBr 2 and SOFC1 are known while the selenyl fluoride, chloride and bromide exist. Thionyl chloride is made from S0 2 and phosphorus pentachloride: S0 2 + PC1 5 -> SOC1 2 + POC1 3 The other thionyl halides are derived from the chloride. Selenyl chloride is obtained from Se0 2 and SeCl 4 . These oxyhalides are stable near room temperature but decompose on heating to a mixture of dioxide, halogen and lower halides. SOF 2 is relatively stable to water, but all the other compounds hydrolyse violently. These compounds have an unshared electron pair on the central element and are pyramidal in structure (Fig. 17.51). In SeOF 2 , FSeF = 92.6° and OSeF = 105.5°. The isoelectronic nitrogen analogue of SOC1 2 , i.e., NSCl^, can be made and has the expected pyramidal shape. The oxyhalides act as weak donor molecules through the lone pairs on the oxygen atoms, and also as acceptors using d orbitals on the sulfur or selenium. SeOX^" complex ions are known for X = F, Cl and Br, and SOF^T is also known and has been predicted to have the expected structure based on a pseudo-trigonal bipyramid, with the sulfur lone pair and oxygen atom in the equatorial plane. Ions M0 2 F~ are known for S, Se and Te, and there are structural differences between the chalcogens. FSO^ is a discrete ionic species, FSeOi~ shows intermolecular bonding through bridging fluorides, while Te0 2 F~ (formed from KF and Te0 2 ) contains the trimeric anión Te 3 O 6 F3~. This contains a puckered six-membered Te 3 0 3 ring, and stereochemically active tellurium lone pairs, giving pseudo-trigonal bipyramidal coordination at Te. For selenium and tellurium the anions M0 2 F 2  $^{\sim}$  are known, together with TeOF^". In SeOCl 2 .2py (py = pyridine) the structure is a square pyramid with a sterically active lone pair. 17.7.5 The II state: the -II state If poly-sulfur compounds are excluded, the II state

is represented by a more limited range of compounds than the IV or VI states, but it is more fully developed than the I state of the nitrogen Group. Tellurium and polonium form readily oxidized monoxides, MO, and a number of dihalides, MX 2 , exist. No difluorides occur (apart from a possible SF 2 ) but the general pattern of stability of the other dihalides resembles that of the tetrahalides, stability decreasing from tellurium to sulfur and from chloride to iodide. TeCl 2 , TeBr 2? PoCl 2 and PoBr 2 are stable. SeCl 2 has only recently been obtained in a pure form (as a red oil) by the reaction of Se with S0 2 C1 2 . SeCl 2 is stable for 24 hours in some solutions, but it decomposes readily in the vapour phase, as does SeBr 2 . SC1 2 , the only sulfur dihalide, decomposes at 60°C and is unstable with respect to dissociation to S 2 C1 2 + C1 2 . No diiodide is known although there is a lower iodide of tellurium, (Tel) n . The lower iodide of sulfur has been shown to be S 2 I 2 : there is no evidence for SI 2 .

TABLE 17.1 5 Oxyacids and oxyanions of sulfur selenium and tellurium

# Sulfur

Sulfur shows coordination numbers up to four, the most common being tetrahedral; S-S bonds are common among the lower acids.

H 2 S0 4 sulfuric acid HS0 4 and S0 4 ~ sulfate Stable, strong, dibasic acid: formed from S0 3 and water. Structure, Fig. 17.47.

H 2 S 2 0 7 pyrosulfuric acid HS 2 Oy and S 2 0y" Strong, dibasic acid: formed from S0 3 and H 2 S0 4 (anions by heating pyrosulfate HS0 4 ), loses S0 3 on heating. Sulfonating agent. Structure, Fig. 17.47. Also anions S 3 0^ and S 5 0^.

H 2 S0 3 sulfurous acid HSOJ and S0 3 ~ sulfites Existence of free acid doubtful. S0 2 +H 2 0 gives a solution containing the anions but this loses S0 2 on dehydration. Reducing and weak, dibasic acid. Structure, pyramidal S0 3 ~ ion; lone pair on S. S 2 C>5~ pyrosulfite No free acid. Formed by heating HSO^ or by S0 2 +S0 3 ~.

### Polythionic acids

H 2 S 2 0 6 dithionic acid S 2 0^" dithionates Acid stable only in dilute solution, anions stable. Formed by oxidation of sulfites and stable to further oxidation, or to
reduction. Strong, dibasic acid, Structure, Fig. 17.50. Sn&l~ (n = 3 to 6) Free acids cannot be isolated; anions formed by reaction of S0 2 and polythionates H 2 S or arsenite. Unstable and readily lose sulfur, reducing Structures contain chains of S atoms, Fig. 17.50.

H 2 S 2 0 4 dithionous acid S 2 0 4  $^{\sim}$  dithionite Acid prepared by zinc reduction of sulfurous acid solution, and salts

(or hypo sulfurous) (called also hyposulfites or hydrosulfites) prepared by zinc reduction of sulfites. Unstable in acid solution, but salts are stable in solid or alkaline media, powerful reducing agents. Decompose to sulfite and thiosulfate. Structure, Fig. 17.52 contains S-S link. S 2 0 3 ~ thiosulfate Prepared in alkaline media by action of S with sulfites. Perfectly stable in absence of acid, but gives sulfur in acid media. Mild reducing agent, as in action with I 2 which gives tetrathionate, S 4 0g~. Structure, p.483, derived from sulfate. S0 2 ~ sulfoxylate Best known as the cobalt salt from CoS 2 0 4 +NH 3 ->CoS0 2 + (NH 4 ) 2 S0 3 . The zinc salt may also exist. Unstable and reducing, structure probably V-shaped.

The peroxy acids H 2 S0 5 and H 2 S 2 0 8 , corresponding to sulfuric acid and pyrosulfuric acid, also exist. Structures are shown in Fig. 17.47.

Selenium

Selenium commonly shows a coordination number of four: a smaller number of selenium acids than sulfuric acids is found as the Se-Se bond

is weaker.

H 2 Se0 4 selenic acid HSe0 4 and Se0 4 ~ selenates Formed by oxidation of selenites. Strong dibasic acid, oxidizing. Similar structures to sulfur compounds. Se 2 U7~ pyroselenate No acid, formed by heating selenates.

H 2 SeO 3 selenous acid HSeO^ and SeO 3 ~ selenite Selenium dioxide solution. Similar to S species, but less reducing and more oxidizing. Structure contains pyramidal SeO 3 ~ ion.

Chain anions of selenium have not been found, but selenium (and tellurium) may form part of the polythionate chain, as in SeS 4 0¿~ and

TeS 4 0¿~, where the Se or Te atoms occupy the central position in the chain

Tellurium

Tellurium, like the preceding elements in this period, is 6-coordinate to oxygen.

H 6 TeO 6 telluric acid TeO(OH)^ and TeO 2 (OH) 4  $\sim$ Prepared by strong oxidation of Te or Te0 2 . Structure is octahedral tellurates Te(OH) 6 , and only two of the protons are sufficiently acidic to be ionized, and then only weakly. The acid and salts are strong oxidizing agents, tellurites Te0 2 is insoluble and no acid of the IV state is formed. Tellurites, and polytellurites, are formed by fusing Te0 2 with metal oxides. Different forms of S 2 F 2 F y trans chain form branched form After considerable confusion, the properties of the fluorides of low oxidation state sulfur are now fairly clear. SF 2 , S 2 F 4 and two isomers of S 2 F 2 exist. SF 2 readily disproportionates into SF 4 and S 8 (probably driven by the high S-S bond energy). It is made from SC1 2 plus KF or HgF 2 under careful conditions: this system also readily yields S 2 F 2 . SF 2 is a V-shaped molecule with bond angle 98°. It forms the unsymmetrical dimer F 3 S-SF. S 2 F 2 exists in the trans chain and in the branched form. In the FSSF form, SS is 189 pm, similar to the distances in S 2 and shorter than HSSH or C1SSC1. In the SSF 2 form, SS is reduced further to 186 pm, the FSS angle is 108° and the FSF angle is 93°, arguing some increased electron density in SS. These species are stable at low temperatures in an inert environment. The FSSF form readily converts to the more stable SSF 2 , which can be heated above 200°C before decomposition. However, decomposition is rapid in presence of species like HF. The complex, SeBr 2 L, where L is tetramethylthiourea, is an example of the rare T-coordination. The BrSeBr angle is 175° and the S atom of the ligand completes the T. A number of planar halide anions, such as SeBr^" and Se 2 Br5~, are known as are mixed oxidation state Se (II)-Se (IV) anions, such as Se 2 Brg∼ and SeaBrfo. The -II state is found in the hydrides, H 2 M, and in the anions, M 2 ~. With the more active metals, sulfur, selenium and tellurium all form compounds which are largely ionic, although they have increasing metallic, and alloy-like, properties as the electronegativity of the metal increases. The tendency to form anions increases from the nitrogen Group (where the evidence for M 3 ~ ions, apart from N 3 ~, is limited), through the oxygen Group (where the M 2  $\sim$  ion is more widely found), to the halogens where the X~ ion is the most stable form for all the elements. This trend in anionic behaviour reflects the increasing electronegativity of the elements, and the greater ease of forming singly charged species over doubly or triply charged ones. 17.7.6 Compounds with an S-S or Se-Se bond Many compounds with S-S bonds are known, together with a smaller range of Se-Se species and an even smaller range of Te-Te species. In this section we cover those compounds with one such bond, together with all the oxygen polysulfur compounds. The remaining catenated species with three or more bonded S or Se are discussed in Section 18.2. Bisulfides, 82"', are formed by reacting sulfides with S and addition of acids vields H 2 S 2 . This has a skew structure similar to H 2 0 2 but with angles at S of 92°. Reacting C1 2 or Br 2 with molten sulfur gives S 2 C1 2 or S 2 Br 2 which are more stable than the corresponding SX 2 and also have the skewX-S-S-X structure with SSX angles about 103°. Selenium analogues, Se 2 X 2 (X = F, Cl, Br), have similar structures. Photolysis of the FE=EF species gives the isomeric form F 2 E-E (E = O, S or Se). H 2 Te 2 has recently been found to be stable in the gas phase. Among the oxides, only S 2 O contains a S-S bond. This compound was, for a long time, reported as SO but the most recent work has established the existence of S 2 0 and suggests that SD is a mixture of S 2 0 and SO 2 . S 2 0 is formed by the action of an electric discharge on sulfur dioxide and it is unstable at room temperature. The structure SSO is proposed. A variety of oxyacids and oxyanions with S-S bonds exists, among which are the polythionic acids, H 2 (0 3 S-S n -S0 3 ) where n varies from 0 to 12, and a miscellaneous group of compounds including thiosulfate, dithionite and pyrosulfite. All these compounds are included in Table 17.15. In sulfur-metabolizing organisms, it would be expected that species representing partial oxidation of sulfur would occur on the path to sulfite and sulfate. It is intriguing to find that chromatographic investigations show the presence of all the polythionates from n = ∖ to 20 in cultures of Thiobacillus ferrooxidans. In the polythionic acids, there is a marked difference in stability between dithionic acid, H 2 S 2 0 6 , and the higher members. As dithionic acid contains no sulfur atom which is bonded only to sulfur, it is much more stable than the other polythionic acids which do contain such sulfurs, see Table 17.15. Dithionates result from the oxidation of sulfites: 2SDi~ + Mn0 2 + 4H 3 0 + -> Mn 2+ + S 2 0^- + 6H 2 0 The structure of the thiosulfate anión, SaOa 2 " and the parent acid may be recovered on acidification. Dithionic acid and the dithionates are moderately stable, and the acid is a strong acid. The structure, 0 3 S-S0 3 , has an approximately tetrahedral arrangement at each

sulfur, with n bonding between sulfur and the oxygen atoms. The reaction of H 2 S and S0 2 gives a mixture of the polythionates from 830°" to Su0 2 6 ~, while specific preparations for each member also exist, as in the preparation of tetrathionate in volumetric analysis by oxidation of thiosulfate by iodine: 2S 2 0^ + 12->S 4 0¿- + 2r These compounds have very unstable parent acids, which readily decompose to sulfur and sulfur dioxide, but the anions are somewhat more stable. The structures are all established as 0 3 S-S n -S0 3 with sulfur chains which resemble those in sulfur polyanions. As with the other examples of sulfur chain compounds, each polythionic acid readily disproportionates to an equilibrium mixture of all the others. Thiosulfate, S2U 3  $^{\sim}$  is formed by the reaction of sulfite with sulfur. The free acid is unstable but the alkali metal salts are well known in photography, volumetric analysis, in other applications such as paper making and as an antidote for cyanide poisoning, since thiosulfate can convert cyanide to nontoxic products via the reaction: CN- + S 2 0i- -> SCNT + S0i~ The thiosulfate ion has been found to have the expected tetrahedral geometry, analogous to sulfate, but with one oxygen replaced by a sulfur atom, and with sulfur-sulfur and sulfuroxygen bond distances of 201 and 147 pm respectively. Exchange studies with radioactive sulfur have also demonstrated the presence of two types of sulfur atom. The structure of the ion with one added H has been determined by Raman spectroscopy supported by calculations. In [HS 2 0 3 ]~ the H is attached to the S, giving the linkage [H-S-S0 3 ]~ showing that the formal S=S bond in [S 2 0 3 ] 2 ~ is easily attacked. Dithionite ions, 8204", result from the reduction of sulfite with zinc dust. The free acid is unknown, and the salts are used in alkaline solution as reducing agents. Dithionite (also called hyposulfite or hydrosulfite) decomposes readily: 2S 2 0 2 -H-H 2 0 -> S 2 0§-+2HSDiand the solutions are also oxidized readily in air. The dithionite ion has the unusual structure shown in Fig. 17.52. The oxygen atoms are in the eclipsed configuration and the S-S bond is very long. The S-O bond lengths show that n bonding exists between the sulfur and oxygen atoms, and there is also a lone pair on each sulfur atom. The S atoms must thus make use of d orbitals and it is proposed that the unusual configuration and the long S-S distance arise from the use of a d orbital. 239 pm 151 pm O sОо

FIG. 17.5 2 The structure of the dithionite ion, ! 17.7.7 Sulfur-nitrogen ring compounds Sulfur and nitrogen form a number of ring compounds, of which the best known is tetrasulfur tetranitride, S 4 N 4 . This is best formed by reacting a 1:1 mixture of SC1 2 and SC1 4 with ammonia. It is a yellow-orange solid which is not oxidized in air. although it can be detonated by shock. The structure is shown in Fig. 17.53. The four nitrogen atoms lie in a plane, and the four atoms of sulfur form a flattened tetrahedron, interpenetrating the N 4 square. Alternatively, the structure may be regarded as an S 8 ring with every second sulfur replaced by a nitrogen. S-S distances are fairly short, 259 pm, showing that there is some weak bonding across the puckered ring between opposite sulfur atoms. The selenium analogue, Se 4 N 4 , has a similar structure with Se-N= 178pm and the long Se- • -Se distance = 274 pm. In the S 4 N^ + cation, the loss of electrons removes the cross-ring bonds. The cation is found in two forms, planar and boat-shaped, where all the S-N bond lengths are equal and the charge is delocalized. Similar planar S 4 N3~ and SsN^ cations with equal bonds are known. A number of other ring compounds exist, including S 4 N^ where the additional N bridges the two S atoms at the top of the molecule, F 4 S 4 N 4 where the substituent F atoms are on 483 S S O N

TABLE 17.16 Properties of the elements of the fluorine Group Element Fluorine Chlorine Bromine Iodine Astatine Symbol F Cl Br I At Oxidation states -I -I, I, III, V, VII -I, I, III, V, VII -I, I, III, V, VII -I I IIP V 1, 1, ill., Coordination numbers 1, (2) 1, 2, 3, 4 1, 2, 3, 5 1, 2, 3, 4, 5, 6, 7 Availability Common Common Common Very rare

THE CHEMISTRY OF ASTATINE

Astatine exists only as radioactive isotopes, all of

which are very short-lived. Work has been done using

either 21 x At (fi = 7.2 h) or 210 At (ti = 8.3 h) and the very

high activity'necessitates working in 10~ 14 M solu

tions, and following reactions by coprecipitation with

iodine compounds. The chemistry of astatine is

therefore little known. Preparation is by the action

of oc-particles on bismuth, for example: 2 <sup>°</sup>9Ri i 4T\_r<sup>^</sup> . 211 A t i 9<sup>°</sup> n 83 bi + 2 He-> 85 At + 30 n Coprecipitation with iodine compounds indicates the existence of the oxidation states shown in Table 17.16. The negative state is probably the At" ion and the positive states, the oxyions, AtO~, AtO^r and AtOi".

Astatine appears to differ from iodine in not giving a VII state, in which it parallels the behaviour of the other heavy elements in its period, and in not forming a cation, At + . Two interhalogens are known for astatine, Atl and AtBr, and there is evidence for polyhalide ions including astatine. It is possible to synthesize organic astatine compounds, RAtO 2 , R 2 AtCl and RAtCl 2 , in the III and V states. The compounds in the commonest state, RAt, correspond to the well-known organic halides in the -1 state. A very wide range of organic groups R have been explored, including biologically important molecules, such as steroids. These have the potential for specific radiotherapy by taking At to the site of a tumour. A more detailed account of the applications of inorganic compounds in medicine is given in Chapter 20. ci Br FIG. 17.5 4 Some properties of the halogens. The radii of the anions, X, are almost identical with the corresponding van der Waals' radii. Notice also, that the electron affinities do not follow a regular trend from fluorine to iodine fiuorocarbons used in all sorts of applications from high-performance lubricants to nonstick frying pans. Simpler members are used as refrigeration liquids and propellants, mostly mixed fluorochloromethanes or ethanes. Chlorine is made by electrolysis of brines and isolated either as C1 2 , as aqueous base solutions containing OC1~ initially and converted to chlorate or perchlorate, or converted with hydrogen to HC1. Principal uses of the element or the oxychloro compounds are in bleaching (wood pulp for paper, textiles) or sterilization (water supply, swimming pools, some stages of sewage treatment, domestic bleaches). Organochlorine compounds in industry are often produced by the action of C1 2 over metal chloride catalysts, especially Fe or Cu. These products, such as vinyl chloride, CH 2 =CHC1, are themselves used largely in polymer formation giving the plastics of commerce (e.g. polyvinyl chloride, PVC). C1 2 is used to make Br 2 from bromides, found in brines or from seawater in general. Bromine is ?! co ^ \*-\* I I ^ J2 £ S E g t\ I CO L Q-> c S O VscOIT\*i5"048512.011.010.09.08.07.06.015. 0 c ii £ 4 -° 1 3. 0 2.0 1.0 0.0 -1.0 -2.0 -3.0 I II III IV oxidation state VI VI I FIG. 17.55 Oxidation state free energies of the halogens. This Group, like the earlier

ones, shows a negative state which decreases in stability from the first to the last member of the Group. The positive states are all fairly similar: bromine has the least stable V and VII states while l v is more stable relative to l v " than is Cl v relative to Cl v "

Oxygen fluorides are discussed in Section

17.7.2. mainly used to prepare organobromine compounds which are used as insecticides, as fire retardants for fibres, as an anti-knock agent in petrol (ethylene dibromide), and in some applications paralleling chlorine in water treatment and sterilization. Iodine is recovered from iodide salts and brines by chlorine oxidation, often with an intermediate stage of iodide concentration; It finds a wide range of uses, mainly as organoiodine compounds, in Pharmaceuticals, photography, pigments, sterilization, dyestuffs and rubber manufacture. Fluorine is the most electronegative element and can therefore exist only in the -I state. The -I state is also the most common and stable state for the other elements, although positive states up to the Group state of VII occur. The positive states are largely found in oxyions and in compounds with other halogens, but iodine does appear to exist in certain systems as the coordinated I + cation. The reactivity of the elements decreases from fluorine to iodine. Fluorine is the most reactive of all the elements and forms compounds with all elements except helium, neon, and argon. In all cases, except with the other rare gases, oxygen and nitrogen, fluorine compounds result from direct, uncatalysed reactions between the elements: the exceptions react in the presence of metal catalysts such as nickel or copper. Chlorine and bromine also combine directly, though less vigorously, with most elements while iodine is less reactive and does not react with some elements such as sulfur. 17.8.2 The positive oxidation states The positive oxidation states occur in the compounds of chlorine, bromine and iodine with oxygen and fluorine, and of the heavier halogens with the lighter ones. The oxides of the elements are shown in Table 17.17.

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TABLE 17.1 7 The oxides of the halogens Average oxidation state I II III IV V VI VII (b = boils d = Chlorine C1 2 0 (b. 2°) C1-C10 2 C10 2 (b. 11°) C1 2 0 6 (b. 203°) C1 2 0 7 (b. 80°) = decomposes, tempe Bromine Br 2 0 (d. -16°) Br-0-Br0 2 (d. -40)°) Br-0-Br0 3 Br 2 0 5 (d. -20°) Br0 3 or Br 3 0 8 (d. 20° Br 2 0 7 (?) ratures in °C) Iodine I 2 0 4 (d. 130°) I 4 0 9 (d. >100°) I 2 0 5 (d. >300°) ) Q

FIG. 17.56 a The structure of the I 4 0i 2 unit in iodine trioxide,

IOs. In the solid these units are linked together through

bridging oxygens from the IO 6 octahedra to the IO 3 trigonal

pyramids Stability of the oxides is greatest for iodine, then chlorine, with bromine oxides the least stable. The higher oxides are rather more stable than the lower ones. Typical preparations are: 2C1 2 + 2HgO -> C1 2 0 + HgCl 2 .HgO (also for Br 2 0) 2KC10 3 + 2H 2 C 2 0 4 -> 2C10 2 + 2C0 2 + K 2 C 2 0 4 + 2H 2 0 (also with sulfuric acid: the method using oxalic acid gives the very explosive C10 2 safely diluted with carbon dioxide). C10 3 , BrO 3 and I 4 0 9 are prepared by the action of ozone while C1 2 0 7 and I 2 U5 are the result of dehydrating the corresponding acids. Iodine oxides are typically isolated from complex mixtures, are polymeric, and decompose to iodine and I 2 0 5 on heating. Many iodine oxide phases been poorly characterized, and some doubt must be cast upon the authenticity of some materials in the absence of good characterization data. The most stable of all the oxides is iodine pentoxide, I 2 0 5 , which is obtained as a stable white solid by heating HIO 3 at 200°C. It dissolves in water to re-form iodic acid, and is a strong oxidizing agent which finds one use in the estimation of carbon monoxide: I 2 0 5 + 5CO->I 2 + 5C0 2 The iodine is estimated in the usual way. Iodine trioxide, with empirical composition IO 3 , is one recent example of an iodine oxide material which has been fully characterized by an X-ray structure determination. The material crystallizes as I 4 Oi 2 units, containing two I0 6 octahedra (with iodine in the VII oxidation state) and two trigonal pyramidal iodines (with iodine in the V oxidation state). I 4 0 12 can thus be viewed as a mixed anhydride of two molecules of H 5 I0 6 [iodine (VII)] and two of HI0 3 [iodine(V)] (Fig. 17.56a). I 2 0 4 contains chains of 10 units which are cross-linked by IO 3 units. The structure of I 4 0 9 is less certain but it has been formulated as I(I0 3 ) 3 . I 2 0 7 has been reported as an orange polymeric solid formed by dehydrating HIO 4 with oleum. The most stable chlorine oxide is the heptoxide which is the anhydride of perchloric acid, HC10 4 . It is a strong oxidizing agent and dissolves readily in water to give perchloric acid. It has the structure 0 3 C1-0-C10 3 with tetrahedral chlorine. C1 2 0 6 is a red oil which melts at 4°C. It is dimeric in carbon

tetrachloride solution but the pure liquid may contain some of the monomer, C10 3 . In the solid, it is ionic, ClOjC10 4 . The ClOj ion is known in a few other compounds with large anions such as ClOjGeF^. It readily decomposes to C1O 2 and oxygen and reacts explosively with organic materials. Like the other chlorine oxides, it can be detonated by shock. In this, it is more sensitive than the heptoxide but more stable than C1 2 0 and C10 2 . Chlorine dioxide is a yellow gas with an odd number of electrons. It detonates readily but is gradually being used on a large scale in industrial processes, for example as a more environmentally friendly bleaching agent. In these processes it is made in situ and always kept well diluted with an inert gas. Notwithstanding the extremely hazardous nature CHAPTER 17 487 147.6 pm 270.8 pm 147.1 pm 115.6 0 ci O o FIG. 17.56 b The structure of chlorine dioxide, CI0 2 , in the solid state. The CIO 2 molecules dimerize via a weak interaction The structures of some bromine oxides Br 2 0 Br 2 O 5 of C10 2 , its molecular structure has been determined in the solid and gaseous states. In the gas phase C10 2 is an angular molecule with an 0-Cl-O angle of 118°. In the solid state, however, C10 2 is dimerized, Fig. 17.56b, though the interactions are relatively weak. C10 2 dissolves freely in water to give initially the hydrate, C10 2 .8H 2 0. On exposure to visible or ultraviolet radiation this gives an HC1 and HC1Ü4 solution. Dichlorine monoxide, C1 2 0 is an orange gas which dissolves in water to give a solution containing hypochlorous acid HOC1. It is a symmetrical angular molecule with a C1-0-C1 angle of 110°. It is powerful oxidizing agent and highly explosive—indeed, most manipulations of C1 2 0 are carried out with a substantial wall between the experimenter and the compound. The mixed oxidation state chlorine oxide, chloryl chloride, C1-C10 2 has also been recently described. This compound decomposes to C10 2 and C1 2 in the gas phase. In solid matrices, C1-C10 2 can be isomerized to Cl-O-Cl-0 and C1-0-0-C1. The bromine oxides are the least stable of all the halogen oxides and all decompose below room temperature, through there is some indication that they may be less explosive than the chlorine analogues. Br 2 0 is dark brown, Br 2 0 3 and Br 2 0 5 are orange and colourless, respectively. It is not clear whether the next oxide has the formula Br0 3 or Br 3 0 8 . This is also colourless and it decomposes in vacuum with the evolution of Br 2 0, leaving a white solid which could possibly be Br 2 0 7 . Reaction of ozone with bromine gives Br 2 0 3 , formulated as bromine brómate, or, under longer reaction times, dibromine pentoxide, Br 2 0 5 . One of the possible compounds having the composition Br0 2 has been recently shown to be bromine perbromate,

Br-0-Br0 3 . The bromine oxides dissolve in water or alkali to give mixtures of the oxyanions. The oxyacids of the halogens are shown in Table 17.18. Most are obtainable only in solution, although salts of nearly all can be isolated. HOP has also recently been established. Hypochlorous acid, HOC1, occurs to an appreciable extent, 30%, in solutions of chlorine in water, but only traces of HOBr and no HOI are found in bromine or iodine solutions. All three halogens give hypohalite on solution in alkali: X 2 + 20H-^XO-+X~+H 2 0 (17.1) K = [X"][XO"]/J 2 = 7  $\times$  10 15 for C1? 2  $\times$  10 8 for Br, 30 for I but the hypohalites readily disproportionate to halide and halate: 3XO-^2X-+X03~ (17.2) with equilibrium constants of 10 27 for Cl, 10 15 for Br and 10 20 for I. This the actual products depend on the rates of these two competing reactions. For the case of chlorine, the formation of hypochlorite by reaction (1) is rapid, while the disproportionation by reaction (2) is slow at room temperatures so that the main products of dissolution of chlorine in alkali are chloride and hypochlorite. For bromine, reactions (1) and (2) are both fast at room temperature so that the products are bromide, hypobromite, and brómate, the proportion of brómate being reduced if the reactions occur at 0°C. In the case

TABLE 17.18 Oxyacids of the halogens Type Name Stability HOX Hypohalous X = F, Cl, Br, I F > Cl > Br > I. All are unstable and are known only in solution. HOXO Halous X = Cl HBr0 2 possibly exists also. HOX0 2 Halic X = Cl, Br, I Cl < Br < I. Chloric and bromic in solution only but iodic acid can be isolated as a solid. HOX0 3 Perhalic X - Cl, Br, I Free perchloric, perbromic and periodic acids occur. Also (HO) 5 IO and FL^Oc forms of periodic acid of iodine, reaction (2) is very fast and iodine dissolves in alkali at all temperatures to give iodide and iodate quantitatively: 3I 2 + OUÏT -> 10^ + 5P + 3H 2 0 The only halous acid definitely established is chlorous acid, HC10 2 , though salts containing the bromite ion Br0 2 are now well defined. An X-ray structure determination on sodium bromite trihydrate confirms the presence of an angular Br0 2 ion with an 0-Br-O angle of 105.3°. HC10 2 does not occur in any of the disproportionation reactions above and is formed by acidification of chlorites. The latter are themselves formed by reaction of C10 2 with bases: 2C10 2 + 20H- -> CICC + C10 3 - + H 2 0 Chlorites are relatively stable in alkaline solution and are used as bleaches. In acid, chlorous acid rapidly disproportionates to chloride, chlorate and chlorine dioxide. For the halic acids, stability is greatest for iodine. Salts of all three acids are well-known and stable, with a pyramidal structure. The 104" ion, containing iodine(V), has recently been reported

in the solid-state compound Ag4(U0 2 )4(I0 3 ) 2 (IO 4 ) 2 0 2 . The 104" ions have a sawhorse geometry, derived from a trigonal bipyramid with one equatorial position empty, and occupied by a lone pair of electrons. The halic acids are stronger acids than the lower ones and are weaker oxidizing agents. All perhalates exist and perchloric acid and perchlorates are well known. HC1Ü4 is the only oxychlorine acid which can be prepared in the free state. It, and perchlorates, although strong oxidizing agents, are the least strongly oxidizing of all the oxychlorine compounds. The perchlorates of many elements exist. The ion is tetrahedral and has the important property of being weakly coordinated by cations. It is thus very useful in the preparation of complexes, as metal ions may be introduced to a reaction as the perchlorates, with the assurance that the perchlorate group will probably remain uncoordinated—contrast this with the behaviour of ions such as halide, carbonate or nitrite which are often found as ligands in the complexes, e.g.: Co 2+ + NH 3 + Cr oxidize } Co(NH 3 )^ + + Co(NH 3 ) 5 Cl 2+ +, etc. but Co 2+ + NH 3 + C1Û4 oxidize ) Co(NH 3 )^ + only After eluding attempts to make it for many years, perbromic acid and its salts were synthesized in 1968. Perbromate, BrO^, was prepared electrolytically, or alternatively by oxidation with XeF 2 , but the most convenient synthesis was found to be oxidation of brómate in alkali by molecular fluorine. Acidification yields perbromic acid which is a strong monobasic acid, stable in solutions up to about 6 M. KBr0 4 contains tetrahedral Br04∼ ions, and this species is predominant in solution with no evidence of a second form as found in periodates. The electrode potentials have been assessed for the reaction XC>4 + 2H+ + 2e^ -> X0 3 - + H 2 0 489

It should be noted that halates, and oxyhalides

generally, are potentially explosive in contact

with oxidizable materials. as 1.23 V for X = C1, 1.76 V for X = Br and 1.64 V for X = I. Perbromate is a somewhat stronger oxidant than perchlorate or periodate, but its oxidizing reactions are sluggish. Thus, the oxidizing power is not the reason for the difficulties found in the synthesis of perbromate. It seems that the preparation from Br(V) requires the surmounting of an activation barrier, and any process proceeding by one-electron additions might have failed because of the instability of the intermediate species. Thus, although the long-standing anomaly about perbromate no longer exists, it is clear that bromine (VII) is less stable in compounds with oxygen than either chlorine (VII) or iodine (VII). To this extent, bromine still reflects the middle element anomaly. Periodic acid and periodates occur, like perrhenates, in 4-, 5- and 6-coordinated forms. Oxidation of iodine in sodium hydroxide solution gives the periodate, Na 2 H 3 I0 0 , and the three silver salts, AgIO 4 , Ag 5 IO 6 and Ag 3 IO 5 , may be precipitated from solutions of this sodium salt under various conditions. Deliquescent white crystals of the acid H 5 I0 6 may be obtained from the silver salt and this loses water in two stages: (HO) 5 IO 8 -^ S H 4 I 2 0 9 ^ C (HO)I0 3 Salts, such as K 4 I 2 0 9 , of the binuclear acid may be obtained. The ^Oc" ion has the 0 3 IO 3 IO 3 structure, of two IO 6 octahedra sharing one triangular face. In the periodates, the IO 6 group is octahedral and the I0 4 group is tetrahedral, as expected. In the related ion [H0 2 I 2 0 8 ] 4  $^{\sim},$  there are two I0 6 octahedra sharing an edge with distance I-OH = 190 pm, 1-0 (terminal) = 181 pm and 1-0 (bridge) =202 pm. In K 3 I0 5 , the 10°" ion has a square pyramidal structure. The iodine oxyanions thus continue the trend, already observed in the earlier members of this period, to become 6-coordinated to oxygen. Positive oxidation states for halogens are also found in the interhalogen compounds, where the lighter halogen is in the -I state and the heavier one in a positive state. A similar situation pertains for the mixed polyhalide ions. Table 17.19 lists these compounds. All the interhalogens of type AB are known, although IF and BrF are very unstable. All the AF 3 and AF 5 types also occur, although, again, some are unstable. Only IF 7 is found in the VII oxidation state, and the only other higher interhalogen is iodine trichloride. All are made by direct combination of the elements under suitable conditions, apart from IF 7 which results from the fluorination of IF 5 . All the compounds are liquids or volatile solids except GIF, which boils at -100°C. Most boiling points fall between 0°C and 100°C. The halogen fluorides are all very reactive and act as strong fluorinating agents. Reactivity is highest for chlorine trifluoride, which fluorinates as strongly as elemental fluorine. Reactivity falls from the chlorine to the bromine and iodine fluorides, and also falls off as the number of fluorine atoms in the molecule increases. BrF 3 and IF 5 are particularly useful as fluorinating agents for the production of fluorides of elements in intermediate oxidation states. These two interhalogens, along with the two iodine chlorides IG1 and IC1 3 , undergo self-ionization and are useful as solvent systems, as discussed in Chapter 6. The anions of these systems, BrF^, IF^, ICl^ and ICC, respectively, are among the polyhalide ions in the table. The cations, BrFj, IF, I + and IClJ, are less familiar but may be isolated by

adding halide ion acceptors to the interhalogen, for example: BrF3 + SbF 5 ^(BrF 2 ) + (SbF 0 )" TABLE 17.19 Interhalogens and polyhalide ions AB AB 3 GIF C1F 3 BrF BrF 3 (IF), (IF 3 ) n BrCl I 2 C1 6 ICI

IBr AB 5 AB 7 (C1F 5 ) IF 7 BrF 5 IPs 3 Br 3 C C1F2 BrF^T BrCC BrC IC12 ClBr^ IBC IBrFIBrCr AB A AB-, AB-, AC1F 4 -C1F 6 - IF 8 - C BrFj BrF 6 If IF 4 " IFo Ig icc I 2 ci 3 IC1 3 F- I 2 Cl 2 Br(IF 3 6 ") tf- ^ IB" B 4 I 2 + also T 2+ ! 4 ^3" ^5" ^2 f AB 4 AB l ClJ Br+ ClFj C1FJ CIF^ Br+ 1+ BrF+ BrF+ BrF+ 1+ (alsol+) FC1+ IF+ IF+ BrClJ IC1+ IBr+ 0 0 231 pm • S b 0 i 0 ci FIG. 17.5 7 The structure of ICI 2 SbCI 6 238 pm 27 0 pm 84° 94 ° 0 ci

FIG. 17.5 8 The structure of iodine trichloride, I 2 CI 6 CI or I The shape of the CIF 4 + and IF 4 + cations Although these compounds are formulated as ions, structural studies show that there may be an interaction between the cation and anión. For example, ICl 2 SbCl 6 , (from IC1 3 and SbCl 5 ) consists of SbCl 6 octahedra and angular IC1 2 units, but with a weak coordination of two of the chlorines in an octahedron to two different iodines to give a chain structure, Fig. 17.57. This structure seems to be quite general, BrFjSbF^ adopting a very similar form to that shown in Fig. 17.57. In both cases, the AB 2 unit may be described as the cation, ABj, forming two further weak bridges to the anión, SbX¿, or as covalent with a very distorted square planar AB 4 unit. The two A-B distances are sufficiently different to make the former description the more acceptable. For FClJ the vibrational spectrum and calculation points to the asymmetric V-shape structure with the linkage C1-C1-F. The other interhalogens of the AB type have properties and reactivities which are roughly the average of the properties of the constituent halogens. Bonding in AB interhalogens has been discussed in Chapter 3. The interhalogens AB 3 are predicted by VSEPR to be planar T-shaped, but there are significant variations in the solid state and depending on the central halogen. Thus,

in the solid, C1F 3 forms a molecular lattice, while BrF 3 interacts with a bromine from another molecule, such that the Br is planar quadrilateral, and reminiscent of the anión BrF^. However, in the recently determined structure of solid IF 3 , the T-shaped IF 3 molecule interacts with iodines of two other IF 3 molecules, giving a pentagonal planar geometry around each iodine atom, reminiscent of the anión IF|~. This results in IF 3 having a polymeric structure, which accounts for its low solubility. BrF 5 and probably the other pentafluorides, are square pyramids of fluorine atoms with the bromine atom just below the plane of the four fluorines of the base. IF 7 is approximately a pentagonal bipyramid. The remaining compound is iodine trichloride which has the dimeric structure shown in Fig. 17.58. A variety of polyhalide ions is known. These are all prepared by the general method of adding halogen or interhalogen to a solution of the halide. The examples with three halogen atoms are linear with the heaviest atom in the middle in the mixed types (although it is not known whether ClBiJ and BrÇ are symmetrical or obey this rule and have structures I-I-Br or Br-Br-Cl). The three-halogen ion, ClBrP, forms a disordered crystal so its structure is not definitely known. The data are best fitted by the arrangement Br-I-Cr with I-C1 longer than Br-I (291 pm and 251 pm respectively). These anions are AB 2 L 3 structures, while the threeatom cations like ClFj have an electron pair less and are V-shaped. Established atom sequences include F-C1-F + and C1-C1-F + . The AB^ compounds are probably all planar ions, with two lone pairs in the remaining octahedral positions. The structures of ICC and BrF 4 have been determined and they are planar. The structures of two ABj cations, IFj and ClFj, with one pair of electrons fewer, have also been determined. These have the same form as SF 4 , which is isoelectronic, and is a trigonal bipyramid with a lone pair in an equatorial position. IF^" and IF¿~, which again differ by one unshared electron pair, present an interesting structural pair. The cation, which has only the six-bond pairs around the iodine, is a regular octahedron as expected. The anión, with a lone pair in addition, is an example of AB 6 L, and resembles some other fluorides with this same number of 491 174.5° 363pm 274pm

305 pm 267pm 290pm 324pm 291 pm

FIG. 17.5 9 Structures of polyiodide ions: (a) I 5 , (b) I 7 ,

(c) \l-, (d) I 9 electrons in forming a distorted octahedron. That is, the lone pair is sterically active, as in XeF 6 or SeF^~. In contrast, however, a recent X-ray structure determination on Cs + BrF^" shows that the BrF^ ion in this species is an almost perfect regular octahedron. In the analogous [Me 4 N] + [C1F 6 ]  $^{\sim}$  the vibrational spectrum is very similar to that of BrF^ so the Cl species also has a regular octahedral geometry. In these cases the lone pair on the central atom is sterically inactive and presumably lies in an s orbital which is poorly screened from the nucleus. The stucture of IFg" has been determined and found to have a square antiprismatic geometry which is overall very similar to the structure of the isoelectronic species XeFg~ (see Section 17.9.4). The other type of polyhalide is limited to iodine and the structures of IJ, 1^, 1^" and Ç are generally irregular chains. These compounds are only stable in presence of large cations such as caesium or ammonium and alkylammonium ions. The structures are shown in Fig. 17.59. The shorter I-I distances are similar to those in iodine but the longer ones correspond to only weak interactions, and all the polyiodides may be regarded as composed of r, I 2 and C groups weakly bonded together. None of the polyiodides survive in solution and they go to iodide, iodine and tri-iodide. The recently discovered mixed species I 2 CC and I 2 Cl 2 Br∼ have bent structures like Ij. There are also a number of compounds which contain both halogen-oxygen and halogen-halogen bonds. These are listed in Table 17.20, along with their ions. Syntheses include fluorination of the corresponding anión. e.g. 0104- + HSO 3 F -> C10 3 F reaction of the interhalogen with OF 2 C1F 5 + OF 2 -» C10F 3 or oxidations as C10 2 F + C1O 2 -> C10 3 F Cations are formed by reactions with fluoride ion acceptors such as MF 5 or BF 3 while addition of F~ gives anions. Most of the species are strong fluorinating and oxidizing agents though perchloryl fluoride, C10 3 F, is relatively unreactive. The species are relatively stable thermally except for C10F, the bromine compounds usually being the least stable. The structures of selected oxyfluoro-halogens are shown in Fig. 17.60 and are those predicted by VSEPR considerations. For I0 2 F 3 the structure is the trimer shown in Fig. 17.61. Polymerization also occurs in place of cation formation when MF 5 species are added to I0 2 F 3 .

(a)

- (b)
- (c)

TABLE 17.2 0 Halogen oxyfluorides and their ions

Oxidation state VII V

III

The commonly

(a) The isomer

(b) I0 2 F 3 .MF 5 Oxypen tafluoridë Dioxytrifluoride C10F 5 C10 2 F 2 + C10 2 F 3 C10 2 F4 Br0 2 F 3 IOF 5 IOF (b)[I0 2 F 3 ] 3 I0 2 F4 Oxytrifluoride ClOFj C10F 3 C10F4 BrOF+ BrOF 3 BrOFJ IOF+ IOF 3 IOF4 Oxyfluoride [C10F] (unstable) used trivial names are indicated. (FO)C10 2 , chloryl hypofluorite, exists but is less stable. etc. are oxygen-bridged polymers. Perhalylfluoride C10 3 F(a) Br0 3 F (I0 3 F) n (72=4?) Halylfluoride ClOj C10 2 F BrOj Br0 2 F (I0j) n I0 2 F C10 2 F^ Br0 2 F;r I0 2 F 2 F IOF 5 CI0 2 F 3 CIO 3 F = 162pm,ab = 103° = 140pm,bb = 115° F'''«n O CIO 2 F 4 XOF 2 F'''/!,,,... «««F Okr F IOF 3 a = 183pm,aa = 192° b = 174pm, be = 98° c = 182 pm XOF 4 X0 2 + (angle approx 120°) CIO 2 F a = 170pm,ab = 102° b = 142pm, bb = 115° CIOF I0 2 F 2 a = 200pm,aa = 180° b = 193pm, bb = 100° FIG. 17.60 Structures of oxyfluoro-halogens: Exact determinations are those for which values of parameters are given. The remainder are compatible with nmr and vibrational spectra

FIG. 17.61 IO 2 F 3 . The suggested structure is a cis bridged

trimer The structure of IOF 6 is of particular interest since it is a seven-electron pair species and one which therefore could adopt one (or more) of a number of possible structures close in energy—see Section 4.2.7 for a discussion on the VSEPR of such species. An X-ray crystallographic study has shown IOFi~ to have a pentagonal bipyramidal structure with the oxygen atom in an apical position. Other electronegative groups may be bonded to halogens in a similar way to F and 0. Thus treatment of BrF 5 with sodium nitrate yields BrOF^, but if LiN0 3 is used, BrOF 3 is evolved and bromine (I) nitrate remains, presumably because the small lithium ion is insufficient to stabilize the large BrOFj anión. The structure is covalent, OBrONO 2 , and the Cl analogue is the same. Action of O 3 yields O 2 BrONO 2 , a bromine (V) compound. It is probable that other oxyion products, especially with Cl or Br in positive oxidation states, are similar covalent species. Although most of the halogen compounds in positive oxidation states are best described as covalent, there is limited evidence available to support an ionic formulation, especially for iodine (III) compounds such as the acetate, I(OCOCH 3 ) 3 , and phosphate, IPO 4 , and the fluorosulfonate, I(SO 3 F) 3 . If a saturated solution of iodine triacetate in acetic anhydride is CIO 2 F 2 + Q I O O

FIG. 17.6 2 The structure of the polymeric cation (Is0 6 )u + .

Two types of iodines are observed: square-planar iodine(lll)

and pyramidal iodine(V) bridged by oxygen atoms, forming a

chain-like structure electrolysed, iodine is found at the cathode and, when a silver cathode is used, Agi is formed and current is used as required by the equation I 3+ + 3e~+Ag^AgI Although no other structural evidence is available, these observations indicate that the compounds could be formulated as containing the I 3+ cation, though such an ion would be expected to interact strongly with the anión and the solids are not to be regarded as simple salts. It is also possible to formulate the oxides I 4 0 9 and I 2 0 4 as r + (I0 3 ) 3 and (IO) + (IOi~). A related polymeric iodine-oxygen cation (i30 6 )^ + has recently been described which has the structure shown in Fig. 17.62. A large number of well-characterized compounds are found which contain the I + ion stabilized by coordination. For example, the pyridine complexes (Ipy 2 ) + X<sup>~</sup> are known for a wide variety of anions, and other lone pair donors coordinate similarly. In all these complexes the iodine appears at the cathode on electrolysis. Chlorine and bromine form analogous, coordinated X + species. In these compounds, the arrangement of the halogen and ligands is linear, L-X-L + . One system which was thought for several years to contain the I + cation has recently been reformulated. This is the blue solution formed by iodine dissolved in oleum and other strong acids (compare Section 6.9). The blue species is also formed by the oxidation of I 2 in IF 5 . It was shown, mainly by work in HS0 3 F, that the blue species is not I + but Ij. Magnetic, conductivity and freezing point depression measurements all fit better for the Ij species. Addition of further iodine gives rise to the Ij and 1^ ions. Both the Ij and the Ç ions tend to

disproportionate to the Ij species. Detailed study of the freezing-point depression shows the equilibrium 2iî^r 251 pm

227pm FIG. 17.6 3 The structure of the BrJ" ion o—o o—o ó—6 Oci O o The shapes of the CI 4 + and CljOj\* ions which lies well to the right at low temperatures. This 1 2 4 + ion can also be synthesized directly in superacid systems. Work with superacid systems has similarly demonstrated the existence of BrJ, BrJ and Br^. The structure of the latter ion has been determined and found to be a zigzag chain of bromines, as shown in Fig. 17.63. In contrast, the most base-sensitive ions, ClJ and C1F + , cannot be formed, even in superacid media, contrary to initial reports. ClJ can, however, be detected spectroscopically in the gas phase. When C1 2 is oxidized with IrF 6 the Cl^ ion is produced (as the IrF^ salt). This chemistry is analogous to the synthesis of OjPtFâ (by oxidation of 0 2 with PtF 0 ) and 'XePtFa' (of unknown structure, from Xe and PtF 6 ). The X-ray structure of Clj" shows a rectangular ion, with two short (194 pm) and two longer (293.6 pm) CI-CI distances. The ion can be envisaged as formed from C1 2 and ClJ by interaction of their n\* systems (a side-on complex with electron donation from C1 2 to ClJ, which stabilizes the latter), and there is a strong similarity with the analogous trapezoidalshaped C1 2 02~ ion formed by oxidation of C1 2 with O^SbF^. The ClJ ion is also known, and has been isolated as salts with various anions. It is interesting that a structural study of BrJ gives Br-Br = 213 pm, compared with 227 pm in neutral Br 2 . This shortening is expected as the electron which is removed in forming the ion comes from an antibonding orbital. 17.8.3 The -I oxidation state In this state, the chemistry of the halogens is well known and many compounds have already been discussed in the earlier sections. Ionic compounds with X~ are formed with the s elements, except beryllium, and in the II and III oxidation states of the transition elements. The change from ionic to covalent character comes further to the left in the Periodic Table for the heavier halogens than for fluorine, as expected from the electronegativities. The region of change is marked by the occurrence of polymeric structures such as A1F 3 , which is a giant molecule with Al-F bonds which can be described as intermediate between ionic and covalent. In the covalent halides, the main differences between the compounds of the different halogens may be ascribed to the differences in size and reactivity of fluorine compared to

PSEUDOHALQGENS OR H&LOGENOIJPS

A number of univalent radicals are found which resem

ble the halogens in many of their properties, and the

name pseudohalogen has been given to these. For

example, consider the cyanide ion, CN". This resembles

the halides in the following respects: (i) it occurs as (CN) 2 —cyanogen—and forms an HX

acid, HCN (ii) it forms insoluble salts with Ag + , Hg + and Pb 2+ (iii) it also gives complex ions of similar formulae to

the halogens, e.g.  ${\rm Co}({\rm CN})^{\rm \sim \prime \prime}$  or  ${\rm Hg}({\rm CN})4^{\rm \sim}$  (iv) it forms covalent compounds and ionic com

pounds with similar ranges of elements as the halogens (v) it gives 'interhalogen' compounds such as ClCN

or ICN. The analogy should not be pressed too far. Thus,

the CN~ ion has different donor and acceptor proper

ties from the halogens, so its transition metal com

plexes differ in stability and reactions. Other radicals with similar properties include cyanate, OCN, thiocyanate SCN, selenocyanate SeCN, and azido-carbondisulfide, SCSN 3 : all these form R 2 molecules. In addition, the ions azide, N~, and tellurocyanide, TeCN~, act as pseudohalides although no molecule, R 2/ is formed. Despite their explosive nature, the halogen azides, XN 3 , have found application in the synthesis of organic azides and related nitrogen compounds. Bromine azide has a zigzag molecular structure, Br-N-N, with Br-N= 190 pm, the central N-N = 123 pm and the outer N-N =113 pm. The BrNN angle is 110° and the NNN one = 1 7 1 °—all parameters very similar to those of BrNCO (Br-N = 186 pm, BrNC= 118°,.NCO= 172°). In contrast, the solid-state structure of IN 3 consists of I-N-I-N chains with each azide bridging two iodines through a single terminal nitrogen. Other iodine azide compounds are the I(N 3 )J cation (analogous to IClJ and hNj, which has been proposed to have an I-I-N-N-N chain structure. the heavier halides. This is often shown in the formation of hexavalent fluorides and tetravalent halides of the rest of the Group, or, similarly, by the formation of 6-coordinated instead of 4-coordinated complexes. Examples include the formation of SF 6 but only SC1 4 , or of CoF¿~ but only

CoClJ. In this oxidation state, the halogens show their strongest resemblance and fluorine fits into place as the most reactive of all. This high reactivity derives in part from the relative weakness of the F-F bond in fluorine (similar effects are found for the O-O and N-N single bonds in hydrogen peroxide and hydrazine). The heat of dissociation of F 2 is only 129.3 kj mol" 1, compared with 237.8 kj mol" 1 for C1 2, 188.9 kj mol" 1 for Br 2 and 147.9 kj mol" 1 for I 2. A value extrapolated from those of the heavier halogens would be about twice the observed F 2 value. The decrease is considerable when it is recalled that most elementhydrogen bond strengths are in the order F > Cl > Br > I. 17.9 The helium Group

There is increasing public concern over the

harmful effects of radon gas, which is found

naturally, accumulating in mines and the base

ments of houses, etc. The elements of the helium Group are termed the rare gases, or the inert or noble (implying unreactive) gases. None of these terms is now particularly appropriate. The elements are rare only by comparison with the very abundant components of the atmosphere, oxygen and nitrogen. In terms of absolute composition of the crust and atmosphere, the lighter elements of this Group are common. Neither are the gases inert, as has recently been shown. Probably the term 'noble gases' is least unsatisfactory but no general agreement has been reached as yet. The IUPAC recommended name is rare gas and this will be used here. The rare gases occur as minor components of the atmosphere, ranging in abundance from argon (0.9% by volume) to xenon (9 parts per million). Helium also occurs in natural hydrocarbon gases in some oilfields and is found occluded in some rocks. In both cases, this helium probably arises from a-particles emitted during radioactive decay. The heaviest member, radon, is radioactive and is found in uranium and thorium minerals, where it is produced in the course of the decay of the heavy elements. The other elements are usually produced by fractional distillation of liquid air. The main properties are given in Table 17.21. The low boiling points and heats of vaporization reflect the very low interatomic forces between these monatomic elements: the rise in these values with atomic weight shows the increasing polarizability of the larger electronic clouds.

TABLE 17.2 1 Properties of the rare gases Element Symbol B.p.(K] Heat of lonization Uses vaporization potential (kj

mor 1 ) (kj mol" 1 ) Helium Neon Argon He Ne Ar Krypton Kr Xenon Xe Radon Rn 4.18 27.1 87.3 120.3 166.1 208.2 0.092 1.84 6.27 9.66 13.68 17.99 2371 2080 1520 1359 1170 1037 Refrigerant at low temperatures: airships Lighting Inert atmosphere for chemical and technical applications Radiotherapy The main isotope of helium is helium-4, and if this is cooled below 2.178 K surprising properties appear. In this form, called helium-II, the viscosity is too low to be detected, the liquid becomes superfluid, and it appears to flow in thin films without friction and is able to flow uphill from one vessel to another. No full theoretical explanation of these phenomena is yet available. Until 1962, all attempts to form compounds of the rare gases had failed. Transient species, such as HHe, had been observed in electric discharges but these had very short lifetimes. The rare gases were also found in solids, such as 3C 6 H 4 (OH) 2 .0.74Kr, but these are not true compounds but dathrates.

## CLATHRATE COMPOUNDS

A clathrate is formed when a compound crystallizes in a rather open 'cage' lattice which can trap suitably sized atoms or molecules within them. An example is provided by pora-quinol (p-C 6 H 4 (OH) 2 ; p-dihydroxy benzene) which, when crystallized under a high pressure of rare gas, forms an open, hydrogen-bonded cage structure which holds the rare gas atoms in compounds like the krypton one above, or like 3C 6 H 4 (OH) 2 .0.88Xe. When the quinol is dissolved or melted, the rare gas escapes. That the clathrates are not true compounds is shown by the large variety of atoms and molecules which may enter the cages. Not

only are quinol clathrates formed by krypton and xenon, but also by O 2 , NO, methanol and many others. The only requirement is that the clathrated species should be small enough to fit the cages and not so small that it can diffuse out: thus helium and neon are too small to form clathrates with p-quinol. Other compounds give clathrates with the rare gases. In particular, the reported hydrates of the rare gases are clathrates of these elements in ice, which crystallizes in an unusually open cage form. Although all clathrates do not involve hydrogen-bonded species, for example the benzene clathrate, Ni(CN) 2 .NH 3 .C 6 H 6 , clathrate formation by hydrogen-bonded molecules is common, as open structures are more readily formed. 17.9.1 Xenon compounds All other attempts to form rare gas compounds, including many studies of possible donor action to yield compounds such as Xe  $\rightarrow \bullet$  BF 3 , failed until 1962. Then Bartlett reported that xenon reacted with PtF 6 to form a compound which he formulated as Xe + (PtF 6 )~. He was led to try this reaction after his discovery of Oj(PtF 6 )~-see Section 15.8—by the consideration that the ionization potential of xenon was close to that (914 kj moP 1 ) of the 0 2 molecule, so that if PtF 0 could oxidize 0 2 to Oj, there was the chance of its oxidizing Xe to Xe + . Further exploration of this field was extremely rapid. A fuller investigation of the reaction led to the discovery of XeF 4 in the second half of 1962. Interest was then concentrated on simple fluorides, oxides, oxyfluorides and species present in aqueous solution. The compounds of these classes are listed in Table 17.22. The existence of XeCl 2 and XeCl 4 has been indicated in Môssbauer experiments using ICC or ICC as sources.

TABLE 17.2 2 Simple rare gas compounds Oxidation state II IV VI VIII Fluorides KrF 2 XeF 2 RnF 2 XeF 4 XeF 6 Oxides Oxyfluorides (XeOF 2 ) XeO 3 XeOF 4 XeO 2 F 2 XeO 4 XeO 3 F 2 (Xe0 2 F 4 ) Acids and salk HXe0 4 Xe(OH) 6 ? Ba 3 Xe0 6 (and HXeO^Ba 2 Xe0 6 (and other salts) similar salts) Compounds in brackets are unstable at room temperature. XeCl 2 exists at low temperatures. XeCl 4 and XeBr 2 exist transiently. These compounds decompose below room temperature, but XeCl 2 was found at 20 K in the products formed by photolysis or by passing Xe and C1 2 through a microwave discharge. Spectroscopic studies suggest that XeCl 2 is linear, though more recent studies have questioned the very nature of this molecule. It has been suggested that XeCl 2 is in fact a van der Waals molecule either linear, of the type Xe- • -CI-CI (analogous to the known van der Waals molecules HeCl 2 , NeCl 2 and ArCl 2 ), or a T-shaped molecule where the Xe atom bridges the CI-CI bond. Liquid xenon and supercritical xenon (see Section 6.11) are finding increasing use as Inert' solvents in which oxidative addition reactions (see Sections 13.9 and 15.7) of highly reactive metal complexes with the C-H bonds of alkanes (usually thought to be fairly inert themselves!) can be investigated. As with the earlier

discussion on noncoordinating anions (Section 17.5.5), a completely noncoordinating solvent is also somewhat of a 'Holy Grail' in chemistry. This is demonstrated by the detection, at low temperatures, of short-lived donor complexes of the type X-M(CO) 5 , where X is either Kr or Xe, and M is either Cr or W. The strength of the W-Xe bond in Xe-W(CO) 5 has been determined to be around 35 kj moP 1 and the complex has a lifetime of about 1.5 minutes at 170 K in liquid Xe. While the xenon-metal bonding in the compounds above is rather weak, much stronger bonding is involved in the remarkable species [AuXe 4 ] 2+ (formed by reduction of AuF 3 with elemental xenon) which has four xenon atoms acting as ligands to an Au 2+ centre. The complex is square-planar with a Au-Xe bond length of about 274 pm; given the generally poor donor ligand abilities of the rare gas atoms, it will be interesting to see if new discoveries in the area of transition metal-xenon species arise in the future. 17.9.2 Preparation and properties of simple compounds Preparations of the fluorides are all by direct reaction under different conditions. Thus a 1:4 mixture of xenon and fluorine passed through a nickel tube at 400°,C gives XeF 2 , a 1:5 ratio heated for an hour at 13 atmospheres in a nickel can at 400°C gives XeF 4 , while heating xenon in excess fluorine at 200 atmospheres pressure gives XeF 6 . Since these original routes were discovered, new routes have been added. In fact, exposing a mixture of xenon and fluorine to sunlight provides a route to XeF 2 which crystallizes on the walls of the reaction vessel. The reaction of Xe and F 2 over a hot filament gives good yields and purity of XeF 6 , and XeF 4 can be correspondingly prepared from 0 2 F 2 and Xe. In the presence of a fluoride ion acceptor such as BF 3 , AgF 2 is also a strong enough oxidant to convert xenon gas to XeF 2 . Most other compounds result on hydrolysis of the fluorides: XeF 6 + H 2 0 -> XeOF 4 + 2HF with an excess of water, XeF 6 + 3H 2 0-+Xe0 3 + 6HF or XeF 4 + H 2 0 ->. Xe + 0 2 +Xe0 3 + HF Here, about half the Xe(IV] disproportionates to Xe and Xe(VI) while the other half oxidizes water to oxygen, forming xenon. Xenon trioxide is hydrolysed in water, probably according to the equilibrium Xe0 3 ^ Xe(OH) 6 Interaction of Xe0 3 and XeOF 4 gives Xe0 2 . The xenon(IV) oxyfluoride, XeOF 2? is formed in a low temperature matrix by reacting Xe with OF 2 , or by the low temperature hydrolysis of XeF 4 . At about -20°C, it disproportionates XeOF 2 ^Xe0 2 F 2 +XeF 2 Xe0 2 F 2 itself gives XeF 2 +0 2 on standing at room temperature. Solution of xenon trioxide, or hydrolysis of the hexafluoride in acid, gives xenates such as Ba 2 Xe0 0 . In neutral or alkaline solution, xenates rapidly disproportionate to perxenates, xenon (VIII). Thus an

overall reaction such as 2XeF 6 + 4Na + + 160HT -> Na 4 Xe0 6 + Xe + 0 2 + 12F~ + 8H 2 0 is observed. The addition of acid to a perxenate yields the tetroxide Ba 2 Xe0 6 + 2H 2 S0 4 -> XeO 4 + 2BaS0 4 + 2H 2 0 The reaction mixture must be kept well cooled as explosive decomposition of Xe0 4 readily occurs. At room temperature, decomposition to Xe+0 2 occurs rapidly. Reaction of XeF 6 with solid Na 4 XeO 6 yields the xenon(VIII) oxyfluoride, Xe0 3 F 2 , together with much XeOF 4 . Xe0 3 F 2 is volatile and was characterized by its mass spectrum. XeOF 4 itself shows some interesting reactions. With CsF, it forms XeOF^ which has a distorted octahedral structure (compare XeF 6 below). With an excess of XeOF 4 a second product forms, [(XeOF 4 ) 3 F]~ where the central F is bonded to the three Xe atoms in a shallow pyramid (angle 116.5<sup>°</sup>) which a very weak bond of 262 pm which contrasts with 190 pm for the Xe-F bond within the XeOF 4 units. An improved procedure for the synthesis of XeOF 4 from XeF 6 employs readily prepared POF 3 as the oxidizing agent. This avoids the generation of explosive Xe0 3 and the byproduct PF 5 is readily removed from the XeOF 4 product because of its higher volatility. The fluorides are all strong oxidizing and fluorinating agents, and most reactions give free xenon and oxidized products: XeF 4 + 4KI -> Xe + 2I 2 + 4KF XeF 2 + H 2 0 -> Xe + ±0 2 + 2HF XeF 4 + Pt -> Xe + PtF 4 XeF 4 + 2SF 4 -> Xe + 2SF 6 The three xenon fluorides are all formed in exothermic reactions (heats of formation of the gases are about 85, 230 and 335 kj mol" 1 for XeF 2 , XeF 4 and XeF 6 respectively). The trioxide is endothermic by 402 kj mol" 1 — largely due to the high dissociation energy of 0 2 . The bond energies of the Xe-F bonds in the fluorides range from 120 to 134 kj mol" 1 from the difluoride to the hexafluoride, a difference which is not far outside the experimental errors. The Xe-0 energy is about 85 kj mol" 1 . The fluorides are all white volatile solids with the volatility increasing from the difluoride to the hexafluoride. The trioxide is also white but nonvolatile, while the tetroxide, Xe0 4 , is a yellow, volatile solid which is unstable at room temperature. The oxyfluorides are also white, volatile solids. While all the early compounds of Xe showed bonds only to F or 0, an increasing number of Xe-N, Xe-C and Xe-Cl bonded species are now known, and many are stable (though chemically reactive) compounds. Often, electronegative groups (often fluorines) are required on the ligands to stabilize them, and this is nicely illustrated by the wide range of compounds with C 6 F 5 -Xe groups discussed later, and shown in Fig. 17.64. (a) C=C X e R = C 2 H 5 , f-butyl, SiMes X = CN, F , Cl XeH F F FIG. 17.6 4 The structures of some compounds containing

xenon-carbon bonds Using matrix isolation techniques at low temperatures, the range of rare gas species which are detectable (though not necessarily stable) can be remarkably extended to include neutral molecules with Xe-H, Xe-I, Xe-Br, Xe-S, Kr-H, Kr-Cl and Kr-C bonds. As an illustration, the species H-Xe-OH has been formed (in a low temperature matrix) from water (dissociated to H and OH radicals using laser radiation) and xenon atoms. As an illustration of an Xe-N bonded species we note the XeF 2 derivative, FXeN(SO 2 F) 2 , which has a linear F-Xe-N unit and a pyramidal N, bonded to the Xe and to 2 S(0) 2 F groups. A number of nitrile-krypton or -xenon compounds of the type RCN-NgF + (Ng = Kr, Xe) are also known. In these, the ligand again generally contains an electron-withdrawing fluorinated R group, such as CF 3 or C 2 F 5 . The unsubstituted krypton ion HCN-KrF + has been reported and, in addition, a theoretical study has suggested that the argon analogue, HCN-ArF + , should be stable and experimentally accessible. These rare gas(II) compounds have the linear structures predicted by VSEPR. Using the fact that xenon-oxygen compounds are less strongly oxidizing than analogous fluorine compounds (in the same xenon oxidation state), compounds containing Xe(VI)-N and Xe(VIII)-N bonds have been prepared in the compounds 0 3 Xe-NCCH 3 and 0 4 Xe-NCCH 3 respectively. In recent years there has been an upsurge of interest in the synthesis of compounds containing xenon-carbon bonds. In these, the organic group generally has a high level of fluorine substitution, and a significant number of the compounds contain the pentafluorophenyl (C 6 F 5 ) group. Some of the xenon compounds of this type which have been prepared are shown in Fig. 17.64. Other than the xenon(IV) compound in Fig. 17.64f, the compounds are of xenon(II) and have a fairly linear geometry at xenon, as illustrated by the acetonitrile complex (Fig. 17.64a), where the C-Xe-N bond angle is 174.5°. Other compounds include ones with two pentafluorophenyl groups (Fig. 17.64b), with cyanide, fluoride or chloride substituents (Fig. 17.64c), or alkynyl or alkenyl groups (Fig. 17.64d and e). 237pm

## FIG. 17.6 5 The structure of the first compound containing a

xenon-carboxylate group The first carbon-bonded compounds of xenon in oxidation state IV have recently been prepared. [C 6 F 5 XeF 2 ] + , with a T-shaped geometry (Fig. 17.64f) has been prepared by the reaction of XeF 4 with C 6 F 5 BF 2 while reaction of XeF 4 with cyanide gives [XeF 4 CN]~. However no compounds of xenon(VI)-carbon bonds have been reported, probably due to the increased oxidizing power of the xenon in combination with oxidizable organic groups. It

is also interesting to note that a pentafluorophenyl xenon derivative is the first example to contain a xenon-carboxylate group, in C 6 F 5 -Xe-OC(0)C 6 F 5 , Fig. 17.65. 17.9.3 Structures The structures of most of the xenon compounds are those predicted by the simple electron pair considerations outlined in Chapter 4, and correspond to the structures of isoelectronic iodine compounds. Some structures are shown in Fig 17.66. 200pm 90 o (a) Xe O F 0 0 FIG. 17.6 6 The structures of xenon compounds: (a) XeF 2 , (b) XeF 4 , (c) XeO 3 , (d) XeOF 4 . These structures are the same as those of the iodine analogues ICf, IFi~ and I0 3 ~ XeO 2 F 2 has a structure like IO 2 Fሪ~ (Fig. 4.6) with a nearly linear F-Xe-F arrangement and an OXeO angle of 106°. XeF is 190 pm and XeO equals 171 pm. XeO 4 is probably a regular tetrahedron, XeO¿~ is octahedral, while the spectrum of XeOF 2 shows it is a further example of the T-shape expected for AB 3 L 2 species: The most interesting structural problem is that presented by XeFo. A monomer would have the AB 6 L structure and would not be expected to be a regular octahedron. In the gas phase, a distorted structure is clearly indicated and three different molecular shapes may be present in equilibrium. However, XeF 6 appears to exist in a polymeric form in the solid and liquid phases. In solution, nmr studies indicate a tetramer, (XeF 6 ) 4 , with equal interaction at room temperature between all the F atoms and the four Xe atoms. This can happen only if the fluorines are rapidly exchanging. The structure of the solid is very complex with the unit cell containing 144 XeF 0 units. These are present as 24 tetramers and 8 hexamers. The configuration of both aggregates is most simply described as XeF^ and F~. The XeF^ units are square pyramids and are linked together by bridges ● ● -F 5 Xe + - ● -F~- ● ● XeF^- ● ●. In the tetramers, the F~ bridges pairs of XeF^" units to form a puckered ring, with unsymmetric bridges of 223 and 260 pm Xe-F~ distances and Xe(F~)Xe angles of 121°. In the hexamer, each F~ bridges three XeF^ units lying symmetrically with Xe-F~ equal to 256 pm and an angle of 119<sup>°</sup>. (Compare these distances with the bonded XeF values given in Fig. 17.68d.) Such bridging would, of course, allow the ready fluorine exchange observed in solution. We note that XeF^" is an AB 5 L, species and the square pyramid is the shape expected for a sterically active lone pair. F F O Xe O • Sb

FIG. 17.67 Structure of the adduct XeF 2 .2SbF 5 The structure

is intermediate between that expected for a full covalent Xe-F

bridging Sb-F bond length = 183 pm. 17.9.4 Reactions with fluorides Xenon fluorides and oxyfluorides react with the fluorides of many elements to give a variety of species. For example, in BrF 5 as solvent XeF 2 + SbF 5 • fl : m = 1 : 1 > /?XeF 2 ./7?SbF 5 1 :2, 2: 1, 1 : 1.5, 1 : 6) By direct reaction, or using SbF 5 as solvent, the species XeF 4 .SbF 5 , XeF 4 .2SbF 5 , XeOF 4 . SbF 5 , XeOF 4 .2SbF 5 and Xe0 2 F 2 .2SbF 5 may be formed. While SbF 5 forms the widest range of species, many other MF 3 , MF 4 , MF 5 and MOF 4 species react similarly, especially with XeF 2 . Under strong fluorinating conditions, XeF 6 .AuF 5 and 2XeF 6 .AuF 5 are formed (containing the unusual Au(V) oxidation state). The crystal structures of a number of these species have been determined, and they are best described as containing the fluoroxenon cation formed by transferring one F~. The cation is then weakly bonded to the anión through a fluorine bridge. The 2:1 adducts contain more complex cations with Xe-F-Xe bridges while 1:2 adducts contain dimeric anions such as Sb 2 F^ whose structure is two octahedra linked by a shared F (Fig. 17.67) Further, weaker interactions occur in some crystals, so that the species contain the cations listed in Table 17.23. The structures of some examples are included in Fig. 17.68. The vibrational spectra are compatible with T-shaped XeFj, pyramidal XeO 2 F + , the AB 4 L type with equatorial oxygen for XeOFj, and square-pyramidal Xe0 2 F 3  $^{\sim}.$  The crystal structure shows Xe0 3 F~ is a polymer of Xe0 3 units (similar to xenon trioxide) bridged through F~ (see Fig. 17.68e). The more complex xenon(VI) ion, Xe 2 F| 1 consists of two square pyramids joined through one of the base corners and this is linked to the AuF^ ion in (Xe 2 F] i) + (AuF 0 )∼ by two more shared fluorines giving an Xe 2 Au triangle with an F in each edge. The Au-F- • -Xe links are very unsymmetrical. A further example of the tendency of Xe(VI) to form complex structures is provided by XeF^AsF^. The XeF^ ion is linked to the AsF^ one in a very unsymmetric bridge Xe- • -F-As (Xe- • -F = 265 pm, F-As = 173 pm) and this XeF^AsF^ unit forms a weak dimer by two pairs of Xe(F) 2 As bridges with long Xe-F distances of 270 and 281 pm. All these weak Xe- • -F interactions should be compared with the van der Waals nonbonding contact distance of 350 pm.

TABLE 17.2 3 Some rare gas ions Oxidation state II IV VI KrF + XeF + RnF + XeF+ XeF^ XeF+ XeF^ XeF2Kr 2 F+ Xe 2 F 3 + Rn 2 F 3 +(?) XeOF^ Xe 2 F+ XeOFj Kr0 2 F+ XeO 3 pXeOF^ XeO 2 F+ XeO 3 Cr XeO 2 F 3 Notes 1. See text for

structures: note especially that there are weak F bonds between cations and fluoroanions. 2. Countercations are usually large M + e.g. Rb + , Cs + , NO + . 3. Counteranions include MF^ (M = P?, As, Sb, V?, Nb, Ta, Ru, Os, Ir, Pt and Au); MF4 (M = B, Al); MF^- (M = Ge, Sn, Ta, Ir, Pd); M 2 F^ (M = As, Sb, Nb, Ta, Ir, Pt); MOF7 (M = W). Crystal structures show that the XeFi ion is a regular square antiprism (compare Fig. 15.5b), in which the lone pair of electrons on the xenon has no detectable effect on the shape of the ion. XeFy has a capped octahedral geometry, with a lengthened bond to the capping fluorine. A crystal structure determination has also been carried out on the XeF^~ ion, and it was found to have a pentagonal planar structure, with the two stereochemically active lone pairs adopting trans-axial positions. CHAPTER 17 THE HELIUM GROUP 501 M = As M = Ru a 18 7 18 7 b 22 1 21 8 c 18 1 19 2 MF(av.) 16 8 18 0 ab 179 <sup>°</sup> 177 <sup>°</sup> be 135 <sup>°</sup> 137 <sup>°</sup> (a) XeF + MFe a = 194 b = 216 ab = 178° XeOS = 123° (b) FXeOSO 3 F SOoF a = 190 b = 214 ab = 178 bb = 151 (c) Xe 2 F 3 + In XeF 5 + RuF 6 I n XeF 6 hexamer tetmmer a 17 9 17 6 18 4 b 18 4 19 8 18 6 ab 79 <sup>°</sup> 80 <sup>°</sup> 77 <sup>°</sup> (d) XeF 5 + a = 177(av.) b = 236 c = 248 aa = 99° (av.) ab = 83° ac = 77° be = 99° (e) (Xe0 3 F-) n FIG. 17.6 8 Structures of some xenon-fluorine species. (All bond lengths are in pm) One of the few compounds to have a bond to Xe from an element other than 0 or F is formed in the reaction 1Q0<sup>°</sup>P "3 ("PC" 0 2 BF 4 +Xe -^ BXeF 3 ^> Xe + BF 3 A planar structure based on XeF 2 with a BF 2 unit replacing one F is indicated. -< In reactions with strong acids, HOY, stepwise substitution of F in XeF 2 occurs: e.g. XeF 2 + HOY -> FXeOY -> Xe(OY) 2 This is known for Y = TeF 5 , SeF 5 , S0 2 F, S0 2 CF 3 , S0 2 CH 3 , C10 2 and CF 3 CO and possibly for NO 2 . Some analogous Xe(IV) and Xe(VI) species also occur. A related synthesis uses the anhydride (Y0) 2 0 as in XeF 2 + P 2 0 3 F 4 -> FXeOPOF 2 -> Xe(OPOF 2 ) 2

A calculation reported in 1987, using He as the most difficult case for compound formation, suggested that a number of species might be sufficiently stable to allow isolation, including (HeCCHe) + and other similar acetylene deriva tives. Also quite stable could be the species HeBeO which could be formed by implanting BeO) into a helium matrix at low temperatures.

Argon, krypton and xenon analogues have been

recently reported. The structure of FXeOY is not dissimilar to the FX+MF 6 species, as shown in Fig. 17.68 a, b. Similarly, Xe(OY) 2 has a linear bridge as in F 5 SeO-Xe-OSeF 5 . In the IV state analogous compounds are also becoming established. Xe(OTeF 5 ) 4 is square planar with Xe-0 = 203 pm. The VI state is represented by 0 2 Xe(OTeF 5 ) 2 and OXe(OTeF 5 } 4 . The first shows the expected five-electron pair structure with equatorial oxygens with distinctly weak double bond repulsion (Xe=0 =173 pm and an 0=Xe =0 angle of 106°). The axial single bond, Xe-OTeF 5 , distance is 202 pm. Reaction of xenon gas with XeF + Sb 2 Fn in SbF 5 solvent gives rise to a green colouration, and it has been shown that the presence of HF is necessary for the reaction to proceed (no reaction was observed when pure HF-free SbF 5 solvent was used). From the solution, the dark green dixenon cation Xe^ crystallizes (with the Sb 4 F 2 ~ 1 ion), with a long Xe-Xe bond length of 308.7 pm. The XeJ cation is isoelectronic with the ion I¿", which is also dark green. 17.9.5 Other rare gas species The only simple compound of krypton is KrF 2 (earlier reported as KrF 4 ). This is thermodynamically unstable and the Kr-F bond energy of about 50 kj moP 1 is the lowest known element-fluorine value. KrF 2 should therefore find use as a very reactive fluorinating agent. The compound is linear, with Kr-F 189 pm, and it decomposes at room temperature at the rate of 10% an hour. Its chemistry is little explored but the 1:1,1:2 and 2:1 adducts with MF 5 (M = Sb, Nb and Ta) are reported. These are formulated as the KrF + or Kr 2 Fj salts of MF^ or M 2 F^, as with the xenon analogues. These species are rather more stable than KrF 2 . Evidence for compounds containing Kr-0 bonds comes from Kr0 2 F + Sb 2 F^, made like the Xe analogue, and Kr(OTeF 5 ) 2 , prepared by the reaction of KrF 2 with B(OTeF 5 ) 3 . KrF 2 , often in conjunction with xenon fluorides, finds application as a powerful fluorinating agent. Thus treatment of Ln(III) compounds yields the Ln(IV) species LnF 4 , LnFy~ and LnOF 2 , not only for the readily oxidized Ce, but also for Ln = Pr, Nd, Tb and Dy (compare Section 11.4). Extrapolating from Kr through Xe would indicate that radon should form a range of compounds. However, all of the isotopes are radioactive, and not much work has been reported since the initial studies some years ago. RnF 2 and the RnF + cation (in the form of salts with SbFi~, BiF¿ and TaF 6

anions) are well-established. A number of other compounds which might be expected are higher fluorides, the oxide Rn0 3 and ions such as Rn0 3 F~ but there is some uncertainty as to their authenticity. It is suggested from the ionization potentials (Table 17.21) that argon, neon and helium are unlikely to form stable compounds corresponding to the xenon and krypton compounds above. However, by using low temperature matrix isolation techniques, (which effectively trap any unstable species formed) the neutral H-Ar-F molecule has recently been identified, and is believed to have predominantly covalent H-Ar and F-Ar bonds, in the ground state. The HArF molecule is stable only at low temperatures in a matrix. This work represents an important milestone in the possible future chemistry of argon, since previously the only species known involving argon were van der Waals adducts or species formed in an excited state. The question then arises as to whether other species, for example ArH + or ArF + , might be obtainable; recent calculations have suggested that the latter might be stable enough to be isolated. In such species, the argon atom can be considered to be acting as an electron pair donor to the extremely strong Lewis acid F + . In this context it is interesting that a number of XHe + species (X = a range of common electron deficient radicals) have been identified in interstellar clouds. However, while species such as XeF + can be formed by fluoride ion abstraction from XeF 2 (plus a powerful Lewis acid such as SbF 5 ), the same route is not available for ArF + due to the extreme instability of ArF 2 . Therefore, routes analogous to the synthesis of NF^ or CIF^, (which have no stable corresponding NF 5 or C1F 7 from which F~ could be removed) must be used. 17.10 Bonding in Main Group compounds: the use of d orbitals The bonding in xenon compounds has been the subject of some controversy which raises the wider question of the degree to which the valence shell d orbitals participate in bonding in any compound where more than four electron pairs surround a Main Group atom. The case of XeF 2 is the simplest to discuss. The two ligands occupy axial positions and three lone pairs occupy equatorial positions in a trigonal bipyramid. To accommodate these five electron pairs requires five orbitals which are formed from the s, the three p and a d orbital on the central atom. But it has been objected that, in the case of xenon, the energy gap between the p and d orbitals is very large, equal to about 960 kj mol" 1 , and it is unlikely that the bond energies are sufficient to compensate for the energy required to make use of a d orbital in such a scheme. Instead, three-centre a bonds between xenon and fluorine are proposed. The molecular axis is taken as the z-axis, as in

Fig. 17.69, and the relevant orbitals are the xenon p z orbital, which contains two electrons, and the p z orbital on each fluorine which hold one electron each (the other six valency electrons on xenon and fluorine fill the s, p x and p y orbitals on each atom, all nonbonding). The three p^ orbitals can be combined to give three G orbitals, centred on the three atoms, one of which is bonding, one nonbonding and one antibonding (Fig. 17.69). The four electrons fill the bonding and nonbonding orbitals to give an overall bonding effect. The position is similar to that in the three-centre B-H-B bond in the boranes, except that there are four electrons instead of two to be accommodated (compare Section 9.5). The cases of XeF 4 and XeF 6 can be explained similarly using xenon p x (or p x and p y for XeF 6 ) orbitals as well as p z in the two cases. Similar descriptions apply to the interhalogen compounds and ions such as ICC, IC1J, BrF 5 , and so on. All these species can be described either in terms of full electron pair bonds, plus nonbonding pairs, by using one or two of the d orbitals, or the use of d orbitals may be avoided by using polycentred molecular orbitals at the price of reducing the bond order. It has been reported that calculations using s and p orbitals only are very successful in reproducing the bond angles and bond lengths found in interhalogen compounds. The theory using three-centred orbitals formed by the p orbitals would predict that XeF 6 , and the isoelectronic IF¿~, should be regular octahedra while the electron pair repulsion theory suggests that these species with seven pairs around the central atoms should be distorted. It is now established that XeF 6 , IF¿ and TeF¿~ are distorted octahedra, while the isoelectronic MK 2 6  $^{\sim}$ species (where M = Se, Te, Pô; X = Cl, Br, I but not F) are undistorted. This again shows the delicate balance which must exist between the various energies making up these two different structures. Recent theoretical work on the general problem of d orbital contributions to bonding in Main Group compounds has made considerable progress. This is mainly because use of large computers has allowed work to be carried out with fewer initial assumptions and approximations. (1 ) In compounds with second row and heavier elements bonded to highly electronegative elements like oxygen and fluorine, there is evidence of substantial d orbital participation in the bonding orbitals. For example, in PF 3 , the population of the phosphorus orbitals is calculated to be: <i bonding 3s 1.51 electrons 3p 1.05 electrons 3d 0.13 electrons TI bonding 3p 0.84 electrons 3d 0.62 electrons Thus, the use of the d orbital gives a small stabilization to the a bonds, but makes a significant contribution to n bonds. Notice that this contribution is made in a molecule with only four electron

pairs on the phosphorus, that is where there are enough s and p orbitals to hold all the valency Pi PX e P 2 F! X e F 2 FIG. 17.6 9 The formation of three-centre bonds in XeF 2 : the constituent alomic orbitals. If we define the positive direction of the p orbital as for the Xe one drawn, the three-centre combinations give the following orbitals bonding ^ =-pi + cp Xe -p2 nonbonding iA=-Pi + P2 antibonding ^=—PI—c'px e + Pz where the constants c and c' are of similar size and the expressions are to be regarded as normalized. The bonding orbital and the nonbonding orbital both contain two electrons. As only one pair of bonding electrons exists between three atoms, the Xe-F bond order is only one-half. XeF 4 may be described similarly using p orbitals in both the x and y directions electrons. In higher oxidation state fluorides and oxides, such as PF 5 , OPF 3 , SF 0 or XeF 6 , there is distinct d orbital involvement in the bonding. This would seem to be supported experimentally by the existence of IF 7 and nonoctahedral MF 6 L species. The test of the calculation is its agreement with experimentally determined ionization or promotion energies (showing the differences between orbital energies) and the agreement between calculated and experimental dipole moments (which reflect the distribution and spatial density of the electron clouds). (2) In compounds where the bonded atoms are of lower electronegativity, like C or H, only a very low d orbital population, of the order of a few percent, is found for the central atom. This has little effect on the calculated energies, but does greatly improve the agreement between calculated and observed dipole moments. That is, the introduction of d orbitals into the calculations has, as its main benefit, a better description of the dispersion of the electrons in space. For further discussion of bonding in compounds of the Main Group elements, see Section 18.9.

## Problems

1 Illustrations of the topics which could be reviewed are: (a) each oxidation state (properties, stability) (b) each coordination number (electron pair counting, stability, extent of distribution) (c) polymeric species (d) element-element bonding (e) PTT-PTT building (f) d orbital participation in Main Group chemistry (g) distinguishing behaviour of first element in a Group.

2 The first dissociation constants K\ of some oxyacids are listed below. Compare with their structures (see also Table 6.2). Find out the values for the other oxyacids of the main Group elements and discuss any anomalies. HN0 2 H 3 P0 4 H 4 P 2 0 7 H 3 As0 3 H 3 As0 3 ^ICT 3 7xl(T 3 3 Compare the oxidation state free energy diagram for Cl with that of Mn. Discuss the similarities and differences and correlate with the chemistry. Extend this comparison to the other halogens and to rhenium. Carry out a similar analysis for other Groups.

4 Plot the first ionization potential against the atomic radius for the p elements across each of the periods. Comment on trends and anomalies. If the sum of the potentials involving all the valence electrons is plotted similarly, do the same trends emerge? 5 Write an essay on Main Group species with ring structures, including the structures of the elements as well as compounds. Compare ring compounds with the corresponding chain species. 6 Survey the structures found for the chlorides of the p elements. Compare and contrast with those of the same formula found for (a) s elements, (b) d elements, (c) f elements. 7 Recently, NaPOa has been isolated at low temperatures as a monomeric species. Discuss its likely structure. What compound or compounds would you expect it to form on warming to room temperature? 8 The structural parameters of some sulfuryl halides (compare Fig. 17.48a) and thionyl halides (Fig. 17.51) are tabulated below. Discuss the variations in bond lengths and angles in terms of VSEPR theory and the relative electron-withdrawing effects of the halogens. S=0 (pm) OSO S-F (pm) XSX S-Cl(Br) (°) (°) (pm) S0 2 F 2 138.6 125 151.4 99 SO 2 FC1 140.7 123 153.8 99 196.4 SOC1 2 141.8 122 77 198.0 SOC1 2 143.9 96 206.8 SOBr 2 145 99 (225) CHAPTER 17

The systematic choimtry given In this chapter is best assimilates! l>y working through rt i& as many ways as posSit>fe< Compare behaviour within toe same

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12

9 Se 2 0 2 F 8 is prepared via SeOF 4 . Predict possible structures for the monomer and dimer. Compare Se 2 0 2 F 8 with other oxyhalides and discuss whether Se-O-Se or Se-F-Se bridging is the more likely. How do your predictions match with the following observed parameters: For Se 2 F 10 0, Se-0-178 pm, SeOSe = 98°, Se- -Se = 267 pm For Se 2 F 8 0 2 , Se-0 = 170 pm, SeOSe = 142°, Se- -Se = 321 pm

10 What structure would you expect for the SÍ40J3~ ion, recently isolated as the silver salt? Compare this with the species of overall formula Si^^Si^^ and Si 4 0fo (compare Section 18.6). What formulae would you find for each of the phosphorus analogues?

11 A bulky cation, I 8  $^{\sim},$  has an almost planar structure  $\smallsetminus$ c ∖ d ∖ c a = 283 pm ab = 174° b = 304pm be = 132° c = 339 pm cd = 168° d = 277 pm (a) Discuss this in terms of the idea that polyiodides can be seen as associations of I 2 and Ç units. (b) Compare with the structure of Cs 2 I 8 shown in Fig. 17.59. In the gas phase, C1F 3 0 shows the following parameters: lengths (pm) Cl-0= 141, Cl-F(l) = 160, C1-F(2) - 171 angles (°) OC1F(1) = 109, OC1F(2) = 95, F(1)C1F(2)= 88andF(2)ClF(2) = 171 Discuss these values in terms of the structure predicted by the VSEPR approach. Compare the values with the related compounds shown in Fig. 17.60. 13 The ClOj ion is bent, with an angle of 119<sup>°</sup> and Cl-0 lengths of 141 pm. In C10 2 the bond is longer, 148 pm, but the angle is similar, 118°. Discuss these observations in terms of the expected bonding. 14 N 2 0 5 , PC1 5 and C1 2 0 6 share the property of being covalent in the gas phase, but forming an ionic solid. Find other examples, from both the d and p blocks. Discuss the various reasons accounting for this behaviour. 15 Discuss the molecular parameters listed below: 16 17 C1F 3 BrF 3 XeF+ M-F eq 160 pm 172 pm 184pm M-F ax 170 pm 181 pm 191 pm Angle (°) 87.5 86.2 81 One compound containing the XeFj" ion has the SbF 0 counterion. Discuss the likely preparation. As the Sb-F distance is 191 pm and there is one of the anión F atoms at 241 pm from Xe, discuss secondary interactions in this compound and compare with related compounds. Discuss the parameters found for SeF 4 and SeOF 2 : for SeF 4 Se-F(a) = 177.1 pm, F-Se-F angle(a) = 100.6° Se-F(b) = 168.2 pm, F-Se-F angle(b) = 169.2° for SeOF 2 Se-0= 157.6 pm, 0-Se-F angle- 105° Se-F= 172.95 pm, F-Se-F angle = 92°

FIG. 19.7 The structure of the ions [AgTe 7 ] 3 " and [HgTe 7 ] 2  $^{\sim}$  CI FIG. 19.8 The structure of the sulfur nitride iridium complex lrCI(CO)(PPh 3 )(S 4 N4) Ph 3 P' C 0 19.3 Fullerenes, nanotubes and carbon 'onions'!—inew forms of elemental carbon 19.3.1 Fullerenes and their metal derivatives It was believed for many years that there were only two well-defined allotropes of the element carbon—the three-dimensional diamond and the planar-sheet structure of graphite. However, the chemistry of carbon has recently taken on a new dimension with the discovery of molecular allotropes such as C 60 (see Section 17.5 and Fig. 5.14d). The discovery of C 60 was a rather serendipitous one. The investigators were looking at carbon-clustering experiments in the gas phase aimed at simulating the chemistry of molecules observed in cold, dark clouds in interstellar space. (The chemistry of outer space is a fascinating subject in itself and a whole range of molecules, such as the polyalkynyl cyanides, HC X N where x is 5, 7 or 9, have been identified. A very brief overview is given in Section 8.7.) The Cj 0 molecular ion was regularly observed as a strong peak in the mass spectra and this led to a closed-shell spheroidal structure being proposed for the C 00 molecule, as illustrated in Fig. 5.15d. (The name Buckminsterfullerene was coined for this new molecule after R. Buckminster-Fuller, the architect who first designed geodesic domes.) Not until 1990 was it found that carbon soots could contain relatively large amounts of fullerenes, predominantly C 60 but also a significant amount of C 70 and larger fullerenes. The fullerenes can be recovered from the soot simply by extracting it with an aromatic hydrocarbon, and chromatography can be used to separate C 60 from C 70 . The availability of macroscopic amounts of C 60 turned it, almost overnight, from what was essentially a curiosity to a material with an enormous number of potential applications. The synthetic procedure for making fullerenes is deceptively simple and essentially involves striking an arc between two graphite electrodes in a low-pressure helium atmosphere. In this regard it is highly surprising that the fullerenes were not discovered much earlier. The procedure is also highly suitable for use in the undergraduate chemistry laboratory and reference to this is made in Appendix A. Since their discovery fullerenes have also turned up in some rather extraordinary places! GOO and C 70 have been detected m fulgurite, a glassy rock formed where lightning strikes the ground—presumably the intense conditions of the lightning strike provide sufficient energy for the fullerenes to form. Fullerenes have also been detected in an impact

crater on a spacecraft which had been in orbit for almost six years. The actual mechanism of formation of these carbon polyhedra is currently the subject of intensive research. The structures of the fullerenes are now well established as there have been many crystallographic determinations of the structures of both the parent fullerenes and their derivatives. The structure of the C 70 molecule, given in Fig. 19.9, is similar to that of C 60 except that it is elongated by insertion of additional hexagons. Again it contains the twelve pentagons necessary to form a closed polyhedron. It was originally envisaged that C 60 was a kind of 'three-dimensional' benzene, or graphite, with fully aromatic properties. The amount of aromatic character is still under scientific debate, through it appears from 3 He nmr data of helium atoms trapped within the fullerene cage that C 70 has the greater amount of aromatic character, based on the diamagnetic shifts of the 3 He resonance. In fact the C 60 molecule contains 'shorter' and 'longer' C-C bonds rather than having all bonds equal which would be expected if the molecule were fully conjugated. This influences the chemistry of these molecules as described later. Not surprisingly, chemists, physicists and materials scientists all around the world rapidly began investigating the properties of the fullerenes almost as if a completely new element had been discovered. Given the pace of developments in this field, we can give only a brief mention of this chemistry here. We do not even attempt to apologise for this since it clearly indicates the vigorous activity which is occurring in this area of chemistry today. A selection of review articles from the recent literature is included in Appendix A and almost any journal in the current literature, particularly Science and Nature, will have the latest findings. FIG. 19.9 The structure of the fullerene C 7( L = pyridine or 4-ferf-butyl pyridine

FIG. 19.10 The structure of the osmylated C 60 derivative

formed on reaction of C 60 with Os0 4 and pyridine f-butyl

pyridine

C 60 contains both 6:6 and 6:5 ring junctions but

no 5:5 ring junctions—a soccerball provides an

extremely useful model!

See Section 16.4 for a discussion on metal
alkene complexes. The Sc 3 N unit in Sc 3 N@C 80 Of particular interest are fluorinated derivatives, such as the perfluorinated C 60 F 0 o. Due to the excellent lubricating properties both of graphite and fluorinated polymers, such as Teflon, it was envisaged that C 60 F 60 would be a 'molecular lubricant', though whether or not such applications arise remains to be seen. The coordination chemistry of the fullerenes was one of the earliest areas studied and it also serves a very useful purpose in structurally characterizing these molecules. The problem lies with the high symmetry of the fullerene molecules which in turn produces rotational disorder of the molecules in the crystal lattice. Making a metal derivative disrupts the symmetry, thereby reducing the probability of disorder. The first metal derivatives prepared were osmylated complexes formed by addition of Os0 4 and pyridine to the C 6 o framework. The complex formed is shown schematically in Fig. 19.10. Very high selectivity is typically observed, with the osmium adding to a 6:6 ring junction where the highest degree of carbon-carbon double bond character exists. This chemistry has also been used to form the first example of an optically active element since the fullerene C 82 is chiral [it contains either a left-handed or a right-handed helical structure). By using Os0 4 with a chiral pyridine ligand, a kinetic resolution of the different enantiomers is achieved. One enantiomer reacts quicker with one form of the base, giving diasteroisomers which can then be separated by physical methods. The osmium can then be removed by reduction with SnCl 2 , giving the resolved enantiomers of C 82 . A range of organometallic derivatives of fullerenes has also been synthesized and in all of these the general properties of the complexes point towards the fullerenes behaving more like electron deficient alkenes than electron rich benezene-like ligands. For example, the electron rich zero-valent platinum-ethylene complex Pt(77 2 -C 2 H 4 )(PPh 3 ) 2 reacts with C 6 o forming the ^ 2 -C 60 complex Pt(^ 2 -C 00 )(PPh 3 ) 2 in which again the platinum bonds to the more reactive 6:6 ring junction. Ouite a wide range of complexes with other metals and fullerenes has been reported. Perhaps the most compelling evidence for the electron deficient character of C 60 comes from ruthenium derivatives. The pentamethylcydopentadienyl complex [Cp\*Ru(NCCH 3 ) 3 ] + contains labile methyl cyanide ligands, which are readily substituted by benzene and most other arenes to form ^-arene complexes: [Cp\*Ru(NCCH 3 ) 3 ] + + arene -» [Cp\*Ru(>7 ó -arene)] + + 3CH 3 CN Compare this hybrid sandwich complex with both ferrocene, Cp 2 Fe, and dibenzenechromium, (^ 2 -C 0 H 6 ) 2 Cr (Section 16.4).

However, when C 6 o is reacted in the same way only one of the three methyl cyanide ligands is displaced from each ruthenium and three rutheniums add to each C 60 : excess [Cp\*Ru(NCCH 3 ) 3 ] + + C 60 [Cp\*Ru(NCCH 3 ) 2 ] 3 C 3 6 + 3CH 3 CN The Sc 2 C 2 unit in Sc 2 C 2 @C 84 This is more reminiscent of the reaction of [Cp\*Ru(NCCH 3 ) 3 ] + with electron deficient alkenes which also only substitute a single methyl cyanide ligand from the ruthenium. In addition to these 'traditional' complexes of fullerenes, another completely different class of metal derivative has been found, though these are much less well studied at the present time. It has been found that the vaporization of a composite rod composed of graphite and a metal oxide, for example La 2 0 3 , under similar conditions as for the preparation of fullerenes, leads to a mixture of fullerenes together with species in which the lanthanum (or other metal atom) is trapped within the fullerene cage. These derivatives have been termed endohedral complexes (in order to form a distinction with the organometallic and osmylated derivatives which are exohedral). The terminology La@C 60 has been coined to describe the endohedral lanthanum complex of C 60 . The properties of these endohedral complexes appear to be somewhat different from those of the parent fullerenes, presumably because the metal causes a significant perturbation in the electronic structure of the fullerene. Larger fullerenes also allow the encapsulation of two or more metal atoms, and in some cases, in combination with other nonmetal atoms. Examples include Y 2 @C 82 and Sc 3 N@C 80 which has a trigonal planar Sc 3 N unit within the fullerene cage and Sc 2 C 2 @C 84 , which has a C 2 unit bridging 2 Sc atoms within the cage. Even reactive (N) and nonreactive (noble gas) atoms can be encapsulated in fullerenes, as illustrated by the dramatic N@C 60 , where the inert inner surface of the fullerene cage protects by isolation the highly reactive nitrogen atom. Further surprises are certain to occur in fullerene chemistry. Another class of metal derivatives of the fullerenes are the fulleride salts formed by reaction of the fullerenes, e.g. C 60 , with alkali metals. The many vacant molecular orbitals of the GOO molecule allow it to accept electrons (from the alkali metals) forming compounds containing the fulleride anions, e.g. M 3 C 60 and M 6 C 00 . The former of these is of current interest since it has been found to superconduct (Section 16.1) at low temperatures. The solid-state structure of M 3 C 60 is also worthy of comment. C 60 itself, as might be expected of a highly symmetrical, pseudo-spherical molecule, packs together quite efficiently and the compound crystallizes in a face-centered cubic lattice (Section 5.6). It will be recalled that for every atom in a close-packed lattice

there are two tetrahedral holes and one octahedral hole per lattice unit, in this case a C 60 molecule. The structure of M 3 C 00 can therefore be derived based on a close-packed C 60 array with all of the octahedral and tetrahedral holes filled by metal ions. 19.3.2 Carbon nanotubes and giant fullerenes In addition to the simple fullerenes C 60 , C 70 , and their larger analogues described above, several other completely new forms of elemental carbon have been discovered. Variations of the procedure for forming fullerenes have led to carbon nanotubes, commonly known as buckytubes. These can be thought of as being formed from a number of sheets of graphite folded round on themselves to form 'nested' cylinders, the ends of which are closed with hemispherical fullerene-like caps, as shown in Fig. 19.11. Yet again, 12 pentagons provide the curvature at the fullerene-like ends of the tubes. A number of novel applications can be envisaged—on heating in air in the presence of lead, the caps are oxidized away, opening the tubes which then act as 'nanopipettes' and fill with the molten lead. Such materials chemistry has enormous potential for the fabrication of nanowires which could be used in electronic devices and the like. Another form of carbon, related to the fullerenes, is the giant nested closed-shell fullerene structures which have been termed 'carbon onions'. It has been found possible to encapsulate moisture-sensitive materials, such as LaC 2 , inside these giant structures, thereby protecting them from atmospheric moisture. In this regard these materials resemble the endohedral fullerene complexes described earlier. 19.3.3 Polyhedral structures formed by other materials: transition metal chalcogenides and metallacarbohedranes The recent discovery that elemental carbon forms molecular species naturally led to the investigation of other materials. The question was asked: 'If graphite, which nominally adopts a layered structure, can be converted into polyhedral forms, such as fullerenes and nanotubes, can the same be done for other layered materials?' Molybdenum and tungsten dichalcogenides MX 2 (X = S or Se) are materials which normally adopt layered structures. These are typified by having strong bonding interactions in two dimensions (in the layer) and weaker interactions in the third direction perpendicular to the layers, as typified by FIG. 19.1 1 Structure of a single carbon nanotube Cbuckytube'). The structure can be considered as a graphite sheet folded to form a cylinder, with fullerene-like hemispherical caps at both ends to eliminate all 'dangling' bonds. Carbon nanotubes prepared in the laboratory typically consist of many concentric, or 'nested', nanotubes. Similar structures are observed for other layered materials, e.g. WS 2

544 the layered silicates talc and mica (Section 18.6). The structure of MoS 2 consists of closepacked sulfide layers with the Mo atoms lying in trigonal prismatic holes between these layers. These slabs then stack by weak forces, as mentioned in Section 15.4. This results in the material finding application as a lubricant. Recent research has found that the MX 2 compounds also form nanotube and nested polyhedral structures akin to those formed by carbon. A recent report has described the formation of similar structures by boron nitride, another layered material isoelectronic and isostructural with graphite. Polyhedral cluster species containing a metal and carbon have also recently been prepared by the laser vaporization of a metal in a hydrocarbon atmosphere. This has been accomplished for a range of metals including Ti, Zr, V, Cr, Fe and Cu and the resulting clusters have been termed metallacarbohedranes or 'met-cars'. The most stable of these is the M 8 C 12 cluster. There is general agreement that these M 8 Ci 2 species form closed-shell polyhedra but the actual structures have been the subject of much recent research and a number of structures have been suggested for them, including a distorted pentagonal dodecahedron containing twelve pentagonal faces, each with two metal and three carbon atoms. Other species which have been detected include the M 14 Ci 3 cluster which has been proposed to have a face-centred cubic structure, essentially a 3 x 3 x 3 ( = 2 7 ) atom fragment of the cubic sodium chloride lattice (Fig. 5.1a). It is noteworthy that this solid-state structure is adopted by a wide number of binary metal carbides (Sections 5.1 and 5.6). Preliminary studies indicate that the M 8 Ci 2 met-cars display a coordination chemistry, and species of the type M 8 C 12 (H 2 0) n (n = 1-8) have been detected in which each metal atom can coordinate a donor ligand, in this case water. Compounds such as these are changing the way that chemists think of materials, and this research is opening up a whole new and exciting area of chemistry. New discoveries and applications of these materials are certain to follow. 19.4 Dendrimeric

In the convergent synthesis method, larger

fragments are initially synthesized, and then

coupled to the core.

FIG. 19.1 2 A schematic diagram of a dendrimer molecule. The

surface of the molecule is derivatized with functional

groups, X molecules 19.4.1 Introduction and dendrimer synthesis Recent years have seen an explosion of interest in a new area of chemistry, that of dendrimeric molecules. The word 'dendrimer' comes from the Greek word for branched; the characteristic features of a dendrimer are a globular structure, formed from a high degree of repeated, ordered branching, coming from a central core. Dendrimers can be considered to be a new class of polymeric molecule, with precisely defined size, shape and chemical properties. Dendrimers can also be considered to be a link between small molecular species and linear polymers, which are classified by their entangled polymer chains and relatively wide molecular weight distribution. The first types of dendrimers were constructed from organic building blocks, but recently there have been many examples of dendrimers constructed from phosphorus, organometallic or coordination complex building blocks. A schematic representation of a dendrimeric molecule is shown in Fig. 19.12. The dendrimer begins with a core molecular unit, around which the dendrimer molecule is constructed. To produce a dendrimer, the core must have at least two reactive functional groups. In the divergent synthesis method, the dendrimer is then built up from the core outwards, by reaction cycles involving addition of one or more reagents, in repeatable synthesis steps. In order for the synthesis to be successful, each reaction step must occur with very high yields. These reaction cycles thus produce different generations of the dendrimer, in the form of concentric layers of repeating structures. The surface of the dendrimer is coated with functional groups (X in Fig. 19.12), which either allow the next generation of the dendrimer to be constructed around it, or alternatively, allow the binding of, e.g., metal complexes, etc. The above points can be illustrated by the synthesis of a small dendrimeric phosphane. Phosphanes are excellent ligands for transition metal centres, and there are potential advantages in using a dendrimeric ligand over smaller analogues, because of the welldefined structure and high molecular weight of a dendrimer. The synthesis, Fig. 19.13, begins with the core species PhPH 2 . By carrying out two cycles of sequential radical CHAPTER 19 P(0)(OR) 2 PhPH 2 catalyst PH 2 P(0)(OR) 2 P(0)(OR) 2 (RO) 2 (0)P X -P(0)(OR) 2 catalyst (RO) 2 (O)P PH 2 P(0)(OR) 2 LiAIH 4 PR 2 FIG. 19.1 3 The synthesis of a dendrimeric phosphane catalyzed addition of the P-H bonds to a vinylphosphonate, CH 2 = CH-P(0)(OR) 2 , followed by reduction with LiAlH 4 (Section 9.5), a small dendrimeric primary phosphane, with terminal PH 2 groups, can be synthesized. To convert this into a dendrimeric tertiary phosphane, the dendrimer PH 2 groups are finally reacted with CH 2 =CH-PR 2 (R = Ph or

Et) to give the final dendrimeric phosphane with terminal PR 2 groups. 19.4.2 Applications The high degree of order of a dendrimer, together with its extensive branching, gives a complex, but ordered, three-dimensional structure. Their use as catalyst supports is one area in which this precise molecular definition is potentially of great benefit. Traditional polymers can be used as soluble catalyst supports. However, the random distribution of catalytic sites and difficulty of removing these materials from the reaction medium limits their effectiveness. It is hoped that dendrimer supported catalysts will retain all of the advantages of homogeneous catalysts (high activity, precisely defined active sites) with the principal advantage of heterogeneous catalysts, which is the ease of recovery from the reaction medium. With dendrimers, the large molecular size and generally spherical shape facilitates recovery of the soluble supported catalyst by simple techniques such as ultrafiltration. As an example, the dendrimeric phosphane ligand of Fig. 19.13, containing surface PR 2 groups, has been reacted with [Pd(MeCN) 4 ] 2+ cations to give a palladiumfunctionalized dendrimer which catalyses the electrochemical reduction of C0 2 to CO, with an activity and selectivity which matches that of analogous monomeric catalysts. ,P(0)(OR) 2 LiAIH 4