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Titanium, Zirconium and Hafnium

21.1 Introduction

In 1791 William Gregor, a Cornish vicar and amateur chemist, examined sand from the local river Helford. Using a magnet he extracted a black material (now called ilmenite) from which he removed iron by treatment with hydrochloric acid. The residue, which dissolved only with difficulty in concentrated sulfuric acid, was the impure oxide of a new element, and Gregor proceeded to discover the reactions which were to form the basis of the production of virtually all TiO_2 up to about 1960. Four years later the German chemist M. H. Klaproth independently discovered the same oxide (or "earth"), in a sample of ore now known to be rutile, and named the element titanium after the Titans who, in Greek mythology, were the children of Heaven and Earth condemned to live amongst the hidden fires of the earth. Klaproth had previously (1789) isolated the oxide of zirconium from a sample of zircon, $ZrSiO_4$. Various forms of zircon (Arabic *zargun*) have been known as gemstones since ancient times. Impure samples of the two metals were prepared by J. J. Berzelius (Sweden) in 1824 (Zr) and 1825 (Ti) but samples

of high purity were not obtained until much later. M. A. Hunter (USA) reduced $TiCl_4$ with sodium in 1910 to obtain titanium, and A. E. van Arkel and J. H. de Boer (Netherlands) produced zirconium in 1925 by their iodide-decomposition process (see below).

The discovery of hafnium was one of chemistry's more controversial episodes[1]. In 1911 G. Urbain, the French chemist and authority on "rare earths", claimed to have isolated the element of atomic number 72 from a sample of rare-earth residues, and named it celtium. With hindsight, and more especially with an understanding of the consequences of H. G. J. Moseley's and N. Bohr's work on atomic structure, it now seems very unlikely that element 72 could have been found in the necessary concentrations along with rare earths. But this knowledge was lacking in the early part of the century and, indeed, in 1922 Urbain and A. Dauvillier claimed to have X-ray evidence to support the discovery. However, by that time Niels Bohr had developed his atomic theory and so was confident that element 72 would be a

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[1] R. T. ALLSOP, *Educ. Chem.* **10**, 222–3 (1973).

member of Group 4 and was more likely to be found along with zirconium than with the rare earths. Working in Bohr's laboratory in Copenhagen in 1922/3, D. Coster (Netherlands) and G. von Hevesy (Hungary) used Moseley's method of X-ray spectroscopic analysis to show that element 72 was present in Norwegian zircon, and it was named hafnium (*Hafnia*, Latin name for Copenhagen). The separation of hafnium from zirconium was then effected by repeated recrystallizations of the complex fluorides and hafnium metal was obtained by reduction with sodium. For rutherfordium ($Z = 104$) see pp. 1280–82.

21.2 The Elements[2]

21.2.1 Terrestrial abundance and distribution

Titanium, which comprises 0.63% (i.e. 6320 ppm) of the earth's crustal rocks, is a very abundant element (ninth of all elements, second of the transition elements), and, of the transition elements, only Fe, Ti and Mn are more abundant than zirconium (0.016%, 162 ppm). Even hafnium (2.8 ppm) is as common as Cs and Br.

That these elements have in the past been considered unfamiliar has been due largely to the difficulties involved in preparing the pure metals and also to their rather diffuse occurrence. Like their predecessors in Group 3, they are classified as type-a metals and are found as silicates and oxides in many silicaceous materials. These are frequently resistant to weathering and so often accumulate in beach deposits which can be profitably exploited.

The two most important minerals of titanium are ilmenite ($FeTiO_3$) and rutile (TiO_2). The former is a black sandy material mined in Canada, the USA, Australia, Scandinavia and Malaysia, while the latter is mined principally in Australia. Zirconium's main minerals are zircon ($ZrSiO_4$)

and baddeleyite (ZrO_2) mined mainly in Australia, the Republic of S. Africa, USA and the former USSR and invariably containing hafnium, most commonly in quantities around 2% of the zirconium content. Only in a few minerals, such as alvite, $MSiO_4.xH_2O$ (M = Hf, Th, Zr), does the hafnium content occasionally exceed that of zirconium. As a result of the lanthanide contraction (p. 1232) the ionic radii of Zr and Hf are virtually identical and their association in nature parallels their very close chemical similarity.

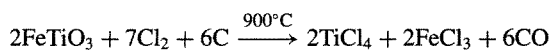## 21.2.2 Preparation and uses of the metals [3]

Viable methods of producing the metals from oxide ores have to surmount two problems. In the first place, reduction with carbon is not possible because of the formation of intractable carbides (p. 299), and even reduction with Na, Ca or Mg is unlikely to remove all the oxygen. In addition, the metals are extremely reactive at high temperatures and, unless prepared in the absence of air, will certainly be contaminated with oxygen and nitrogen.

In 1932 Wilhelm Kroll of Luxembourg produced titanium by reducing $TiCl_4$ with calcium and then later (1940) with magnesium and even sodium. The expense of this process was a severe deterrent to any commercial use of titanium. However, the metal has a very low density (~57% that of steel) combined with good mechanical strength and, in fact, when alloyed with small quantities of such metals as Al and Sn, has the highest strength:weight ratio of any of the engineering metals. Accordingly, about 1950, a demand developed for titanium for the manufacture of gas-turbine engines, and this demand has rapidly increased as production and fabrication problems have been overcome. Its major uses are still in the aircraft industry

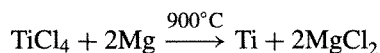[2] R. J. H CLARK, Chap. 32, pp. 355–417, and D. C. BRADLEY and P. THORNTON, Chap. 33, pp. 419–90, in *Comprehensive Inorganic Chemistry*, Vol. 3, Pergamon Press, Oxford, 1973.

[3] *Kirk–Othmer Encyclopedia of Chemical Technology*, 4th edn. Interscience. New York. For Ti, See Vol. 24, 1997, pp. 186–349; for Zr, See Vol. 25, 1998, pp. 853–96; for Hf, See Vol. 12, 1994, pp. 861–81.

for the production of both engines and airframes, but it is also widely used in chemical processing and marine equipment. Current world production capacity is estimated to exceed 120 000 tonnes pa though actual production is less than this. The Kroll method still dominates the industry: in this ilmenite or rutile is heated with chlorine and carbon, e.g.:

$$2FeTiO_3 + 7Cl_2 + 6C \xrightarrow{900°C} 2TiCl_4 + 2FeCl_3 + 6CO$$

The $TiCl_4$ is fractionally distilled from $FeCl_3$ and other impurities and then reduced with molten magnesium in a sealed furnace under Ar,

$$TiCl_4 + 2Mg \xrightarrow{900°C} Ti + 2MgCl_2$$

Molten $MgCl_2$ is tapped off periodically and, after cooling, residual $MgCl_2$ and any excess of magnesium are removed by leaching with water and dilute hydrochloric acid or by distillation, leaving titanium "sponge" which, after grinding and cleaning with aqua regia (1:3 mixture of concentrated nitric and hydrochloric acids), is melted under argon or vacuum and cast into ingots. The use of sodium instead of magnesium requires little change in the basic process but gives a more readily leached product. This yields titanium metal in a granular form which is fabricated by somewhat different techniques and has been preferred by some users.

Zirconium, too, is produced commercially by the Kroll process, but the van Arkel-de Boer process is also useful when it is especially important to remove all oxygen and nitrogen. In this latter method the crude zirconium is heated in an evacuated vessel with a little iodine, to a temperature of about 200°C when ZrI_4 volatilizes. A tungsten or zirconium filament is simultaneously electrically heated to about 1300°C. This decomposes the ZrI_4 and pure zirconium is deposited on the filament. As the deposit grows the current is steadily increased so as to maintain the temperatures. The method is applicable to many metals by judicious adjustment of the temperatures. Zirconium has a high corrosion resistance and in certain chemical plants is preferred to alternatives such as stainless

steel, titanium and tantalum. It is also used in a variety of alloy steels and, when added to niobium, forms a superconducting alloy which retains its superconductivity in strong magnetic fields. The small percentage of hafnium normally present in zirconium is of no detriment in these cases and may even improve its properties, but a further important use for zirconium is as a cladding for uranium dioxide fuel rods in water-cooled nuclear reactors. When alloyed with ~1.5% tin, its corrosion resistance and mechanical properties, which are stable under irradiation, coupled with its extremely low absorption of "thermal" neutrons, make it an ideal material for this purpose. Unfortunately, hafnium is a powerful absorber of thermal neutrons (600 times more so than Zr) and its removal, though difficult, is therefore necessary. Solvent extraction methods, taking advantage of the different solubilities of, for instance, the two nitrates in tri-*n*-butyl phosphate or the thiocyanates in hexone (methyl isobutyl ketone) have been developed and reduce the hafnium content to less than 100 ppm. The neutron absorbing ability of hafnium is not always disadvantageous, however, since it is the reason for hafnium's use for reactor control rods in nuclear submarines. Hafnium is produced in the same ways as zirconium but on a much smaller scale. For rutherfordium see p. 1281.

21.2.3 Properties of the elements

Table 21.1 summarizes a number of properties of these elements. The difficulties in attaining high purity has led to frequent revision of the estimates of several of these properties. Each element has a number of naturally occurring isotopes and, in the case of zirconium and hafnium, the least abundant of these is radioactive, though with a very long half-life ($^{96}_{40}Zr$, 2.76%, 3.6×10^{17} y; $^{174}_{72}Hf$, 0.162%, 2.0×10^{15} y).

The elements are all lustrous, silvery metals with high mps and they have typically metallic hcp structures which transform to bcc at high temperatures (882°, 870° and 1760°C for Ti, Zr and Hf). They are better conductors of

Table 21.1 Some properties of Group 4 elements

Property		Ti	Zr	Hf
Atomic number		22	40	72
Number of naturally occurring isotopes		5	5	6
Atomic weight		47.867(1)	91.224(2)	178.49(2)
Electronic configuration		$[Ar]3d^24s^2$	$[Kr]4d^25s^2$	$[Xe]4f^{14}5d^26s^2$
Electronegativity		1.5	1.4	1.3
Metal radius/pm		147	160	159
Ionic radius (6-coordinate)/pm	M(IV)	60.5	72	71
	M(III)	67.0	—	—
	M(II)	86	—	—
MP/°C		1667	1857	2222 (or 2467)
BP/°C		3285	4200	4450
ΔH_{fus}/kJ mol^{-1}		18.8	19.2	(25)
ΔH_{vap}/kJ mol^{-1}		425 ($\pm$11)	567	571 ($\pm$25)
ΔH_f (monatomic gas)/kJ mol^{-1}		469 ($\pm$4)	612 ($\pm$11)	611 ($\pm$17)
Density (25°C)/g cm^{-3}		4.50	6.51	13.28
Electrical resistivity (20°C)/μohm cm		42.0	40.0	35.1

heat and electricity than their predecessors in Group 3 but are not to be regarded as "good" conductors in comparison with most other metals. The enthalpies of fusion, vaporization and atomization have also increased, indicating that the additional d electron has in each case contributed to stronger metal bonding. As was noticed in comparing groups 3 and 13, similarly for groups 4 and 14, the d electrons of the first group contribute more effectively to the metal–metal bonding in the bulk materials than do the p electrons of the heavier members of the latter group (Ge, Sn, Pb). Figure 21.1 illustrates the consequent discontinuous increases in mp, bp and enthalpy of atomization in passing from C

and Si to Ti, Zr and Hf, rather than to Ge, Sn and Pb.

The mechanical properties of these metals are markedly affected by traces of impurities such as O, N and C which have an embrittling effect on the metals, making them difficult to fabricate.

The effect of the lanthanide contraction on the metal and ionic radii of hafnium has already been mentioned. That these radii are virtually identical for zirconium and hafnium has the result that the ratio of their densities, like that of their atomic weights, is very close to Zr:Hf = 1:2.0. Indeed, the densities, the transition temperatures and the neutron-absorbing abilities are the only common properties of these two elements which differ
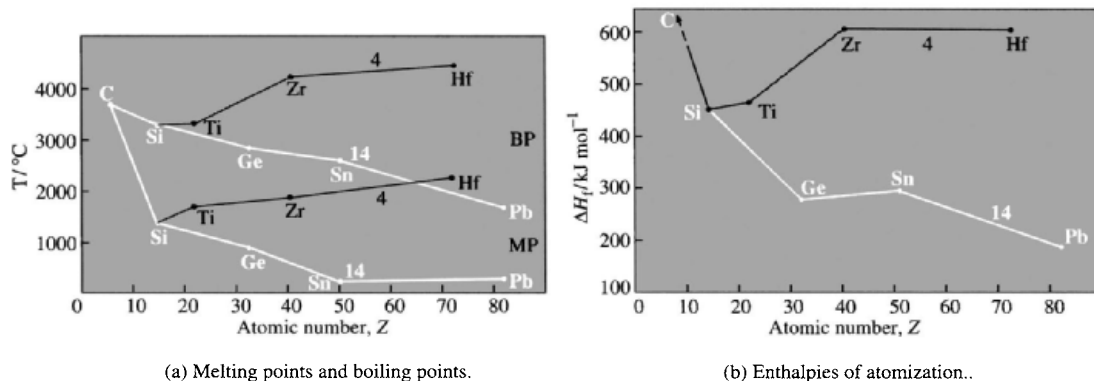

(a) Melting points and boiling points.

(b) Enthalpies of atomization..

Figure 21.1 Trends in some properties of elements of Groups 4 and 14.

significantly. This close similarity of second and third members is noticeable in all subsequent groups of the transition elements but is never more pronounced than here.

21.2.4 Chemical reactivity and trends

The elements of this group are relatively electropositive but less so than those of Group 3. If heated to high temperatures they react directly with most non-metals, particularly oxygen, hydrogen (reversibly), and, in the case of titanium, nitrogen (Ti actually burns in N_2). When finely divided the metals are pyrophoric and for this reason care is necessary when machining them to avoid the production of fine waste chips. In spite of this inherent reactivity, the most noticeable feature of these metals in the massive form at room temperature is their outstanding resistance to corrosion, which is due to the formation of a dense, adherent, self-healing oxide film. This is particularly striking in the case of zirconium. With the exception of hydrofluoric acid (which is the best solvent, probably because of the formation of soluble fluoro complexes) mineral acids have little effect unless hot. Even when hot, aqueous alkalis do not attack the metals. The presence of oxidizing agents such as nitric acid frequently reduces the reactivity of the metals by ensuring the retention of the protective oxide film.

The chemistry of hafnium has not received the same attention as that of titanium or zirconium, but it is clear that its behaviour follows that of zirconium very closely indeed with only minor differences in such properties as solubility and volatility being apparent in most of their compounds. The most important oxidation state in the chemistry of these elements is the group oxidation state of +4. This is too high to be ionic, but zirconium and hafnium, being larger, have oxides which are more basic than that of titanium and give rise to a more extensive and less-hydrolysed aqueous chemistry. In this oxidation state, particularly in the case of the dioxide and tetrachloride, titanium shows many similarities with tin which is of much the same size. A large

number of coordination compounds of the M^{IV} metals have been studied[4] and complexes such as $[MF_6]^{2-}$ and those with O- or N- donor ligands are especially stable.

The M^{IV} ions, though much smaller than their triply charged predecessors in Group 3, are, nonetheless, sufficiently large, bearing in mind their high charge, to attain a coordination number of 8 or more, which is certainly higher than is usually found for most transition elements. Eight is not a common coordination number for the first member, titanium, but is very well known for zirconium and hafnium, and the spherical symmetry of the d^0 configuration allows a variety of stereochemistries.

Lower oxidation states are rather sparsely represented for Zr and Hf. Even for Ti they are readily oxidized to +4 but they are undoubtedly well defined and, whatever arguments may be advanced against applying the description to Sc, there is no doubt that Ti is a "transition metal". In aqueous solution Ti^{III} can be prepared by reduction of Ti^{IV}, either with Zn and dilute acid or electrolytically, and it exists in dilute acids as the violet, octahedral $[Ti(H_2O)_6]^{3+}$ ion (p. 970). Although this is subject to a certain amount of hydrolysis, normal salts such as halides and sulfates can be separated. Zr^{III} and Hf^{III} are known mainly as the trihalides or their derivatives and have no aqueous chemistry since they reduce water. Table 21.2 (p. 960) gives the oxidation states and stereochemistries found in the complexes of Ti, Zr and Hf along with illustrative examples. (See also pp. 1281–2.)

M–C σ bonds are not strong and, as might be expected for metals with so few d electrons, little help is available from synergic π bonding: for instance, of the simple carbonyls only $Ti(CO)_6$ has been reported, and that only on the basis of spectroscopic evidence. However, as will be seen on p. 972, the discovery that titanium compounds can be used to

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[4] C. H. McAuliffe and D. S. Barratt, Chap. 31, pp. 323–61, and R. J. Fay, Chap. 32, pp. 363–451, in *Comprehensive Coordination Chemistry*, Vol. 3, Pergamon Press, Oxford, 1987.

Titanium Dioxide as a Pigment (See page 961)

Of all white pigments, TiO_2 is now the most widely used: the impressive growth in demand is shown in Table A:[5]
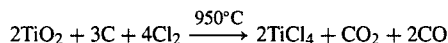
Table A   Annual world production of TiO_2

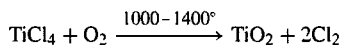| Year	1925	1937	1975	1993
TiO_2/tonnes	5000	100 000	2 000 000	3 730 000

Its major use is in the manufacture of paint, and other important uses are as a surface coating on paper and as a filler in rubber and plastics.

The value of TiO_2 as a pigment is due to its exceptionally high refractive index in the visible region of the spectrum. Thus although large crystals are transparent, fine particles scatter light so strongly that they can be used to produce films of high opacity[†]. Table B gives the refractive indices of a number of relevant materials. In the manufacture of TiO_2 either the anatase or the rutile form is produced depending on modifications in the process employed. Because of its slightly higher refractive index, rutile has a somewhat greater opacity and most of the TiO_2 currently produced is of this form.

In addition to these optical properties, TiO_2 is chemically inert which is why it displaced "white lead", $2PbCO_3.Pb(OH)_2$: in industrial atmospheres this formed PbS (black) during the production of or weathering of the paint and was also a toxic hazard. Unfortunately the naturally occurring forms of TiO_2 are invariably coloured, sometimes intensely, by impurities, and expensive processing is required to produce pigments of acceptable quality. The two main processes in use are the *sulfate process* and the *chloride process* (Fig. A, p. 960), which account for approximately 56% and 44% respectively of total world production. The principal reactions of the chloride process are:

$$2TiO_2 + 3C + 4Cl_2 \xrightarrow{950°C} 2TiCl_4 + CO_2 + 2CO$$

and

$$TiCl_4 + O_2 \xrightarrow{1000-1400°} TiO_2 + 2Cl_2$$

It is most economical when high-grade ores are used, becoming less economical with poorer feed materials containing iron, because of the production of chloride wastes from which the chlorine cannot be recovered. By contrast the sulfate process cannot make use of rutile which does not dissolve in sulfuric acid, but is able to operate on lower grade ores. However, the capital cost of plant for the sulfate process is higher, and disposal of waste has proved environmentally more difficult, so that most new plant is designed for the chloride process.

The physical properties of the base pigments produced from both processes are further improved by slurrying in water and selectively precipitating on the finely divided particles a surface coating of SiO_2, Al_2O_3, or TiO_2 itself.

Table B   Refractive indices of some pigments and other materials

Substance	Refractive index	Substance	Refractive index	Substance	Refractive index
NaCl	1.54	$BaSO_4$	1.64–1.65	Diamond	2.42
$CaCO_3$	1.53–1.68	ZnO	2.0	TiO_2(anatase)	2.49–2.55
SiO_2	1.54–1.56	ZnS	2.36–2.38	TiO_2(rutile)	2.61–2.90

Panel continues

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[5] R. S. DARBY and J. LEIGHTON, in *The Modern Inorganic Chemicals Industry*, pp. 354–74, Special Publication No. 31, (1977), The Chemical Society, London. *Metals and Minerals Ann. Rev.*, 75–6 (1992).

[†] The smaller the particle size, the lower the wavelength at which maximum scattering occurs. Thus, ultrafine (20–50 nm) TiO_2 is used as a UV filter in skin care and cosmetic products. (See V. P. S. JUDIN, *Chem. Br.* **29**, 503–5 (1993).)
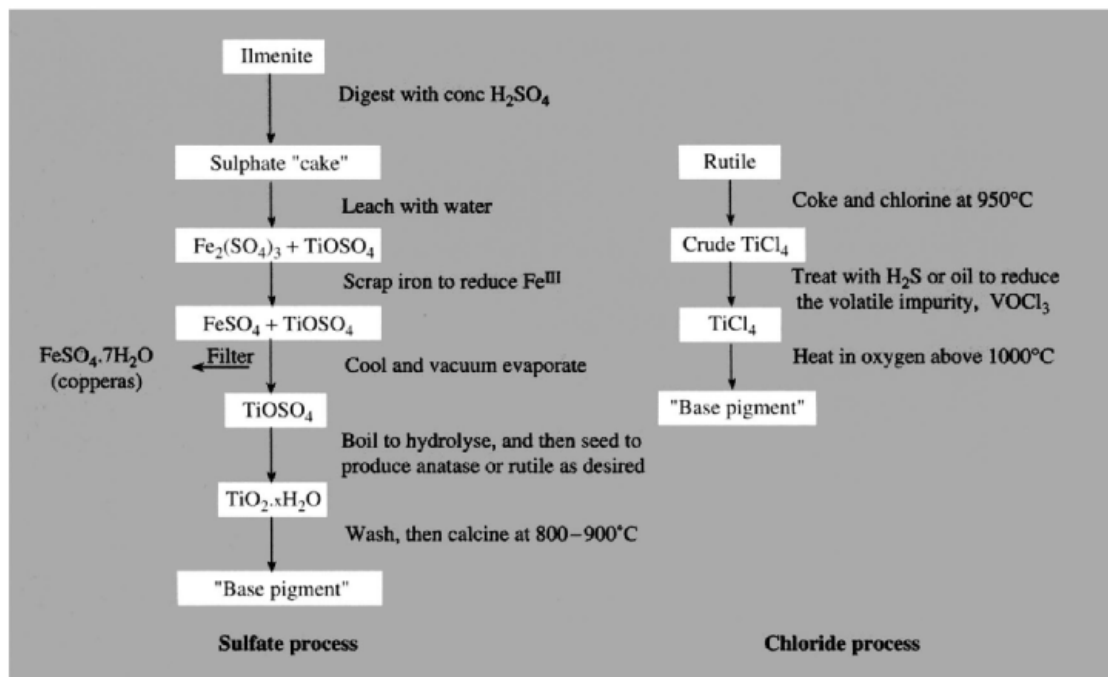
Figure A   Flow diagrams for the manufacture of TiO_2 pigments.

Table 21.2   Oxidation states and stereochemistries of titanium, zirconium and hafnium

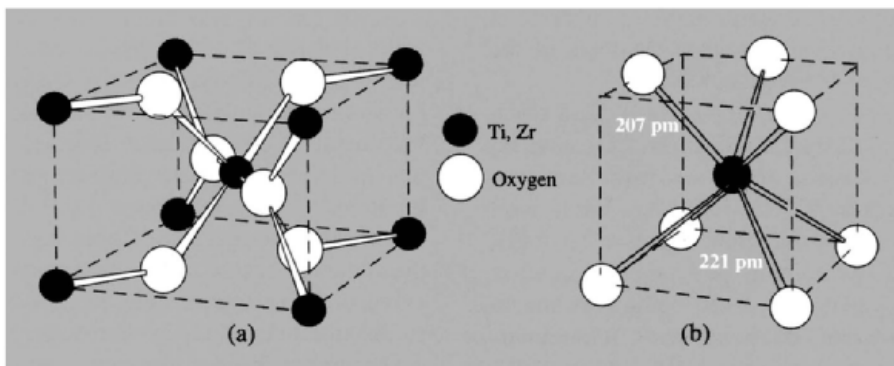| Oxidation state	Coordination number	Stereochemistry	Ti	Zr/Hf
-1 (d^5)	6	Octahedral	$[Ti(bipy)_3]^-$	$[Zr(bipy)_3]^-$
0 (d^4)	6	Octahedral	$[Ti(bipy)_3]$	$[Zr(bipy)_3]$
2 (d^2)	6	Octahedral	$TiCl_2$	Layer structures and clusters
	12	—	$[Ti(\eta^5\text{-}C_5H_5)_2(CO)_2]$	$[M(\eta^5\text{-}C_5H_5)_2(CO)_2]$
3 (d^1)	3	Planar	$[Ti\{N(SiMe_3)_2\}_3]$	
	5	Trigonal bipyramidal	$[TiBr_3(NMe_3)_2]$	
	6	Octahedral	$[Ti(urea)_6]^{3+}$	ZrX_3 (Cl, Br, I), HfI_3
4 (d^0)	4	Tetrahedral	$TiCl_4$	$ZrCl_4(g)$ (solid is octahedral)
	5	Trigonal bipyramidal	$[TiOCl_2(NMe_3)_2]$	—
		Square pyramidal	$[TiOCl_4]^{2-}$	—
	6	Octahedral	$[TiF_6]^{2-}$	$[ZrF_6]^{2-}$, $ZrCl_4(s)$
	7	Pentagonal bipyramidal	$[TiCl(S_2CNMe_2)_3]$	$[NH_4]^+{}_3[ZrF_7]^{3-}$
		Capped trigonal prismatic	$[TiF_5(O_2)]^{3-}$	$[Zr_2F_{13}]^{5-}$
	8	Dodecahedral	$[Ti(\eta^2\text{-}NO_3)_4]$	$[Zr(C_2O_4)_4]^{4-}$
		Square antiprismatic	—	$[Zr(acac)_4]$
	11	—	$[Ti(\eta^5\text{-}C_5H_5)(S_2CNMe_2)_3]$	$[Zr(\eta^5\text{-}C_5H_5)(S_2CNMe_2)_3]$
	12	—	—	$[M(\eta^3\text{-}BH_4)_4]$

Figure 21.2   (a) The tetragonal unit cell of rutile, TiO_2. (b) The coordination of Zr^{IV} in baddeleyite ZrO_2; the 3 O atoms in the upper plane are each coordinated by 3 Zr atoms in a plane, whereas the 4 lower O atoms are each tetrahedrally coordinated by 4 Zr atoms.

catalyse the polymerization of alkenes (olefins) turned organo-titanium chemistry into a topic of major commercial importance and has produced an extensive chemistry. The organometallic chemistry of Zr and Hf, though less developed than that of Ti, has grown rapidly in recent years.

21.3 Compounds of Titanium, Zirconium and Hafnium

The binary hydrides (p. 64), borides (p. 145), carbides (p. 299) and nitrides (p. 417) are hard, refractory, nonstoichiometric materials with metallic conductivities. They have already been discussed in relation to comparable compounds of other metals in earlier chapters.

21.3.1 Oxides and sulfides

The main oxides are the dioxides. In fact, TiO_2 is by far the most important compound formed by the elements of this group, its importance arising predominantly from its use as a white pigment (see Panel, p. 959). It exists at room temperature in three forms — rutile, anatase and brookite, each of which occurs naturally. Each contains 6-coordinate titanium but rutile is the most common form, both in nature and as produced commercially, and the others transform into it on heating. The rutile

structure is based on a slightly distorted hcp of oxygen atoms with half the octahedral interstices being occupied by titanium atoms. The octahedral coordination of the titanium atoms and trigonal planar coordination of the oxygen can be seen in Fig. 21.2. This is a structure commonly adopted by ionic dioxides and difluorides where the relative sizes of the ions are such as to favour 6-coordination (i.e. when the radius ratio of cation:anion lies in the range 0.73 to 0.41).[6] Anatase and brookite are both based on cubic rather than hexagonal close packing of oxygen atoms, but again the titanium atoms occupy half the octahedral interstices. TiO_2 melts at $1892 \pm 30°C$ when heated in an atmosphere of O_2; when heated in air the compound tends to lose oxygen and then melts at $1843 \pm 15°C$ ($TiO_{1.985}$).

Though it is unreactive, rutile can be reduced with difficulty to give numerous nonstoichiometric oxide phases, the more important of which are the Magnéli-type phases Ti_nO_{2n-1} ($4 \leq n \leq 9$), the lower oxides Ti_3O_5 and Ti_2O_3, and the broad, nonstoichiometric phase TiO_x ($0.70 \leq x \leq 1.30$). The Magnéli phases Ti_nO_{2n-1} are built up of slabs of rutile-type structure with a width of $nTiO_6$ octahedra and with adjacent slabs mutually related by a crystallographic shear which conserves oxygen atoms by an increased sharing

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[6] A. F. WELLS, *Structural Inorganic Chemistry*, 5th edn., Chap. 7, pp. 312–19, Oxford University Press, Oxford, 1984.

between adjacent octahedra. Ti_4O_7 is metallic at room temperature but the other members of the series tend to be semiconductors.

Of the lower oxides Ti_3O_5 is a blue-black material prepared by the reduction TiO_2 with H_2 at 900°C; it shows a transition from semiconductor to metal at 175°C. Ti_2O_3 is a dark-violet material with the corundum structure (p. 243); it is prepared by reacting TiO_2 and Ti metal at 1600°C and is generally inert, being resistant to most reagents except oxidizing acids. It has a narrow composition range ($x = 1.49-1.51$ in TiO_x) and undergoes a semiconductor-to-metal transition above ~200°C.

TiO, a bronze coloured, readily oxidized material, is again prepared by the reaction of TiO_2 and Ti metal. It has a defect rock-salt structure which tolerates a high proportion of vacancies (Schottky defects) in both Ti and O sites and so is highly nonstoichiometric[7] with a composition range at 1700°C of $TiO_{0.75}$ to $TiO_{1.25}$. This range diminishes somewhat at lower temperatures and, at equilibrium below about 900°C, various ordered phases separate with smaller ranges of composition-variation, e.g. $TiO_{0.9}-TiO_{1.1}$ and $TiO_{1.25}$ (i.e. Ti_4O_5). In this latter compound the tetragonal unit cell can be thought of as being related to the NaCl-type structure: there are 10 Ti sites and 10 oxygen sites but 2 of the Ti sites are vacant in a regular or ordered way to generate the structure of Ti_4O_5. A high-temperature (>3000°C) form of TiO has been prepared with the unusual feature of Ti^{2+} in a trigonal prismatic array of oxygen atoms.[7a]

Finally, oxygen is soluble in metallic titanium up to a composition of $TiO_{0.5}$ with the oxygen atoms occupying octahedral sites in the hcp metal lattice: distinct phases that have been crystallographically characterized are Ti_6O, Ti_3O and Ti_2O. It seems likely that in all these reduced oxide phases there is extensive metal–metal bonding.

In the case of zirconium and hafnium there is little evidence of stable phases other than MO_2, and at room temperature ZrO_2 (baddeleyite) and the isomorphous HfO_2 have a structure in which the metal is 7-coordinate (Fig. 21.2(b)). ZrO_2 has at least two more high-temperature modifications (tetragonal above 1100°C and cubic, fluorite-type, above 2300°C) but it is notable that, presumably because of the greater size of Zr compared to Ti, neither of them has the 6-coordinate rutile structure. ZrO_2 is unreactive, has a low coefficient of thermal expansion, and a very high melting point (2710 ± 25°C) and is therefore a useful refractory material, being used in the manufacture of crucibles and furnace cores. However, the phase change at 1100° severely restricts the use of pure ZrO_2 as a refractory because repeated thermal cycling through this temperature causes cracking and disintegration — the problem is avoided by using solid solutions of CaO or MgO in the ZrO_2 since these retain the cubic fluorite structure throughout the temperature range. ZrO_2 has also recently been produced in fibrous form suitable for weaving into fabrics, as already mentioned for Al_2O_3 (p. 244), and its chemical inertness and refractivity — coupled with an apparent lack of toxicity — can be expected to lead to increasing applications as an insulator and for the filtration of corrosive liquids. Production of ZrO_2 concentrates in 1991 was about 870 000 t, Australia being the most important source.

The sulfides have been less thoroughly examined than the oxides but it is clear that a number of stable phases can be produced and nonstoichiometry is again prevalent (p. 679). The most important are the disulfides, which are semiconductors with metallic lustre. TiS_2 and ZrS_2 have the CdI_2 structure (p. 1211) in which the cations occupy the octahedral sites between alternate layers of hcp anions.

21.3.2 Mixed (or complex) oxides

Although the dioxides, MO_2, are notable for their inertness, particularly if they have been heated, fusion or firing at high temperatures (sometimes up to 2500°C) with the stoichiometric

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[7] D. J. M. BEVAN, Chap. 49, pp. 453–540 in *Comprehensive Inorganic Chemistry*, Vol. 3, Pergamon Press, Oxford, 1973.

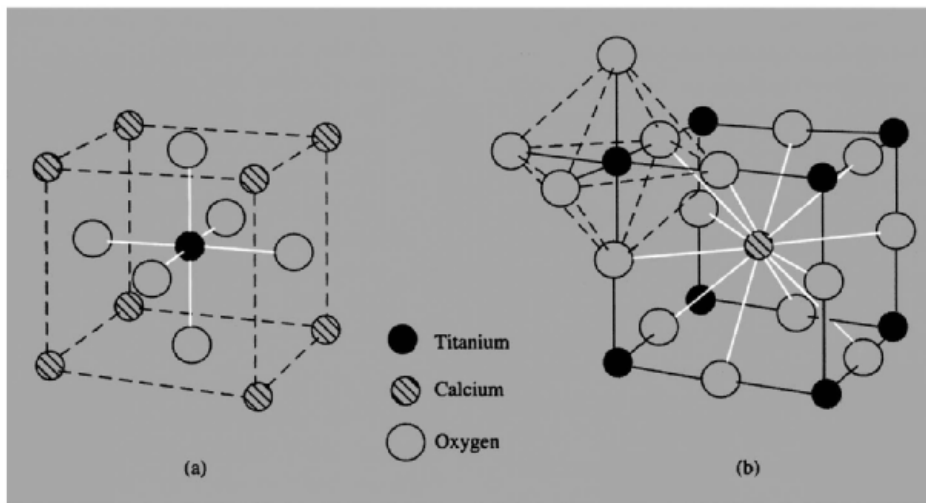[7a] S. MÖHR and H. MÜLLER-BUSCHBAUM, *Z. anorg. allg. Chem.* **620**, 1175–8 (1994).

Figure 21.3 Two representations of the structure of perovskite, $CaTiO_3$, showing (a) the octahedral coordination of Ti, and (b) the twelve-fold coordination of Ca by oxygen. Note the relation of (b) to the cubic structure of ReO_3 (p. 1047).

amounts of appropriate oxides produces a number of "titanates", "zirconates", and "hafnates". The titanates are of two main types: the orthotitanates $M_2^{II}TiO_4$ and the metatitanates $M^{II}TiO_3$. The names are misleading since the compounds almost never contain the discrete ions $[TiO_4]^{4-}$ and $[TiO_3]^{2-}$ analogous to phosphates or sulfites. Rather, the structures comprise three-dimensional networks of ions which are of particular interest and importance because two of the metatitanates are the archetypes of common mixed metal oxide structures.

When M^{II} is approximately the same size as Ti^{IV} (i.e. M = Mg, Mn, Fe, Co, Ni) the structure is that of *ilmenite*, $FeTiO_3$, which consists of hcp oxygens with one-third of the octahedral interstices occupied by M^{II} and another third by Ti^{IV}. This is essentially the same structure as corundum (Al_2O_3, p. 243) except that in that case there is only one type of cation which occupies two-thirds of the octahedral sites.

If, however, M^{II} is significantly larger than Ti^{IV} (e.g. M = Ca, Sr, Ba), then the preferred structure is that of *perovskite*,[8] $CaTiO_3$. This

can be envisaged as a ccp array of calcium and oxygen atoms, with the former regularly disposed, and the titanium atoms then occupying octahedral sites formed by oxygen atoms only and so being as remote as possible from the calciums (Fig. 21.3). The Ba^{II} ion is so large and expands the perovskite lattice to such an extent that the titanium is too small to fill the octahedral interstice which accommodates it. This leads to ferroelectric and piezoelectric behaviour as discussed in Chapter 3 (p. 57). In consequence, $BaTiO_3$ has found important applications in the production of compact capacitors (because of its high permittivity) and as a ceramic transducer in devices such as microphones and gramophone pick-ups. For such purposes it compares favourably with Rochelle salt (sodium potassium tartrate, $NaKC_4H_4O_6$) in terms of thermal stability, and with quartz in terms of the strength of the effect.

$M_2^{II}TiO_4$ (M = Mg, Zn, Mn, Fe, Co) have the *spinel* structure ($MgAl_2O_4$, p. 248) which is the third important structure type adopted by many mixed metal oxides; in this the cations occupy both octahedral and tetrahedral sites in a ccp array of oxide ions. Ba_2TiO_4, although having the same stoichiometry, is unique amongst titanates in that

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[8] A. RELLER and T. WILLIAMS, *Chem. Br.*, **25**, 1227–30 (1989).

it contains discrete $[TiO_4]^{4-}$ ions which have a somewhat distorted tetrahedral structure.

High-temperature reduction of Na_2TiO_3 with hydrogen produces nonstoichiometric materials, Na_xTiO_2 ($x = 0.20-0.25$), called titanium "bronzes" by analogy with the better-known tungsten bronzes (p. 1016). They have a blue-black, metallic appearance with high electrical conductivity and are chemically inert (even hydrofluoric acid does not attack them).

"Zirconates" and "hafnates" can be prepared by firing appropriate mixtures of oxides, carbonates or nitrates. None of them are known to contain discrete $[MO_4]^{4-}$ or $[MO_3]^{2-}$ ions. Compounds $M^{II}ZrO_3$ usually have the perovskite structure whereas $M_2^{II}ZrO_4$ frequently adopt the spinel structure.

21.3.3 Halides

The most important of these are the tetrahalides, all 12 of which are known. The titanium compounds (Table 21.3) show an interesting gradation in colour, the charge-transfer band moving steadily to lower energies (i.e. absorbing increasingly in the visible region of the spectrum) as the anion becomes more easily oxidized (F^- to I^-) by the small, highly polarizing titanium cation. The larger Zr^{IV} and Hf^{IV}, however, do not have the same polarizing effect and their tetrahalides are all white solids; the fluorides are involatile but the other tetrahalides sublime readily at temperatures in the range 320–430°C.

Table 21.3 Some physical properties of titanium tetrahalides

Compound	Colour	MP/°C	BP/°C
TiF_4	White	284	—
$TiCl_4$	Colourless	−24	136.5
$TiBr_4$	Orange	38	233.5
TiI_4	Dark brown	155	377

Though numerous preparative methods are possible besides the direct action of the halogen on the metal, convenient general procedures are as follows:

tetrafluorides by the action of anhydrous HF on the tetrachloride;

tetrachlorides and tetrabromides by passing the halogen over the heated dioxide in the presence of a reducing agent such as carbon (this reaction is central to the chloride process for manufacturing TiO_2, p. 959);

tetraiodides by the iodination of the dioxide with aluminium triiodide at a temperature of 130–400° depending on the metal ($3MO_2 + 4AlI_3 \longrightarrow 3MI_4 + 2Al_2O_3$).

Not all the structures have been determined but in the vapour phase all the tetrahalides of titanium and probably all those of zirconium and hafnium have monomeric, tetrahedral structures. In the solid, TiF_4 is a polymer consisting of corner-sharing $\{TiF_6\}$ octahedra,[8a] but the other tetrahalides of titanium retain the tetrahedral configuration around the metal even in the solids. The larger zirconium exhibits higher coordination numbers. Thus solid MF_4 contain 8-coordinate (square antiprismatic) metal atoms while the tetrachlorides and bromides are polymers consisting of zigzag chains of edge-sharing $\{MX_6\}^{2-}$ octahedra.

All the tetrahalides, but especially the chlorides and bromides, behave as Lewis acids dissolving in polar solvents to give rise to series of addition compounds; they also form complex anions with halides. They are all hygroscopic and hydrolysis follows the same pattern as complex formation, with the chlorides and bromides being more vulnerable than the fluorides and iodides. $TiCl_4$ fumes in and is completely hydrolysed by moist air ($TiCl_4 + 2H_2O \longrightarrow TiO_2 + 4HCl$); a variety of intermediate hydrolysis products, such as the oxochlorides $MOCl_2$, can be formed with aqueous HCl of varying concentration. Even in conc HCl, $ZrCl_4$ gives $ZrOCl_2.8H_2O$. This contains the tetrameric cation $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$ in which the 4 zirconium atoms are connected in a ring by 4 pairs of OH^- bridges and each zirconium atom is dodecahedrally coordinated to 8 oxygen atoms. The fluorides are less susceptible

8a H. BIALOWONS, M. MÜLLER and B. G. MÜLLER, *Z. anorg. allg. Chem.* **621**, 1227–31 (1995).

to hydrolysis and, though aqueous HF produces the oxofluorides, MOF_2, the hydrates $TiF_4.2H_2O$, $MF_4.H_2O$, and $MF_4.3H_2O$ (M = Zr, Hf) can be produced. Rather curiously the trihydrates of ZrF_4 and HfF_4 actually have different structures, though both contain 8-coordinated metal atoms. The zirconium compound is essentially dimeric $[(H_2O)_3F_3Zr(\mu\text{-}F)_2ZrF_3(H_2O)_3]$ with dodecahedral Zr, whereas the hafnium compound consists of infinite chains of octahedral $[>HfF_2(H_2O)_2(\mu\text{-}F)_2]$ with the third water molecule held in the lattice.

Besides being important as an intermediate in one of the processes for making TiO_2, $TiCl_4$ is also used to produce Ziegler–Natta catalysts (p. 972) for the polymerization of ethylene (ethene) and is the starting point for the production of most of the commercially important organic titanium compounds (in most cases these are actually titanium alkoxides rather than true organometallic compounds). The iodides MI_4 are all utilized in the van Arkel–de Boer process for producing pure metals (p. 956).

All the trihalides except HfF_3 have been prepared,[†] the most general method being the high-temperature reduction of the tetrahalide with the metal, though a variety of other methods have been used especially for the titanium compounds. Since the tetrahalides are quite stable to reduction, lower halides are not easily prepared in a pure state, incomplete reactions and the presence of excess metal being common. Apart from TiF_3, which, as expected for a d^1 ion, has a magnetic moment of 1.85 BM at room temperature, and only shows signs of magnetic interactions below about 60 K,[9] all compounds have low magnetic moments, indicative of appreciable M–M bonding. They are coloured, halogen-bridged polymers in which one third of the octahedral interstices of an hcp lattice of halide ions is occupied by metal atoms. In the cases of α-$TiCl_3$ and α-$TiBr_3$ this takes the form of the "BiI_3" structure which is comprised of layers of edge-sharing

octahedra; the remainder adopt the "β-$TiCl_3$" structure, comprised of chains of face-sharing octahedra.[10] In most, if not all, of the latter cases M–M bonds occur between pairs of metal atoms as a result of distortions leading, in the case of ZrI_3 for instance,[11] to alternate Zr–Zr distances of 317.2 and 350.7 pm. TiF_3 also differs in being stable in air unless heated whereas the others show reducing properties; indeed, ZrX_3 and HfX_3 reduce water and so have no aqueous chemistry, but aqueous solutions of TiX_3 are stable if kept under an inert atmosphere. Hexahydrates $TiX_3.6H_2O$ are well known and the chloride is notable in that, like its chromium(III) analogue, it exhibits hydrate isomerism, existing as violet $[Ti(H_2O)_6]^{3+}Cl_3^-$ and green $[TiCl_2(H_2O)_4]^{+}$-$Cl^-.2H_2O$.

TiX_2 (X = Cl, Br, I) have been prepared by reduction of TiX_4 with Ti metal and are black solids with the CdI_2 structure (p. 1211) but their low magnetic moments again indicate extensive M–M bonding. They are very strongly reducing and decompose water. Ti_7X_{16} (X = Cl, Br) have also been prepared. They are black crystalline solids sensitive to hydrolysis and oxidation and can be regarded as being composed of octahedrally coordinated Ti^{IV} and Ti^{II} in the ratio of 1:6 (i.e. $TiCl_4.6TiCl_2$) with the bivalent metal ions arranged in triangular groups involving Ti–Ti bonds. Incorporation of KCl in the chloride reaction mix yields[12] the structurally related KTi_4Cl_{11} but the structural diversity of reduced Ti halides does not yet match that of Zr.

Products of the high temperature (typically 750–850°C) reduction of ZrX_4 (X = Cl, Br, I) with Zr metal in various proportions, have provided intriguing structural problems. Black phases initially thought to be ZrX_2 and made up of Zr_6X_{12} clusters, isostructural with the well-known $[M_6X_{12}]^{n+}$ clusters of Nb and Ta, (p. 992), were subsequently shown to contain

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[†] ZrF_3 may also be doubted (see p. 150 of D. SMITH, *Inorganic Substances*, Cambridge Univ. Press, Cambridge, 1990).

[9] R. HOPPE and ST. BECKER, *Z. anorg. allg. Chem.* **568**, 126–35 (1989).

[10] See pp. 167 and 196 of U. MÜLLER, *Inorganic Structural Chemistry*, 2nd edn., Wiley, New York, (1992).

[11] A. LACHGAR, D.S. DUDIS and J.D. CORBETT, *Inorg. Chem.* **29**, 2242–6 (1990).

[12] J. ZHANG, R.Y. QI and J.D. CORBETT, *Inorg. Chem.* **30**, 4794–8 (1991).

impurity atoms situated inside the Zr_6 octahedra which they actually stabilize. The materials are correctly formulated as $Zr_6X_{12}Z$ and, if alkali metal halides are incorporated in the reaction mix a whole series of phases based on the $[Zr_6X_{12}Z]$ cluster unit is obtained, of which the chlorides and iodides have so far been most thoroughly studied. Z is most commonly H, Be, B, C or N (dark orange to red products), but may also be Cr, Mn, Fe or Co (green, blue or purple products). In all cases the same basic $Zr_6X_{12}Z$ cluster unit is involved, though several structure types result from the differing ways in which these are connected.[13] In most cases it appears that stability is attained when 14 electrons are available for cluster bonding (i.e. total number of valence electrons from Zr_6 and Z, adjusted for overall charge, less 12 required by X^-_{12}) where Z is a main-group element, but 18 electrons where Z is a transition element. It has been suggested that the presence of Z is *essential* for the stabilisation of these clusters, but $Zr_6Cl_{12}(PMe_2Ph)_6$ appears to consist entirely of empty Zr_6Cl_{12} clusters with a phosphine attached externally to each Zr atom.[14]

By contrast, ZrCl and ZrBr, also prepared by the high temperature reduction of ZrX_4 with the metal, appear to be genuine binary halides. They are comprised of hcp double layers of metal atoms surrounded by layers of halide ions, leading to metallic conduction in the plane of the layers, and they are thermally more stable than the less reduced phases. ZrI has not been obtained, possibly because of the large size of the iodide ion, and, less surprisingly, attempts to prepare reduced fluorides have been unsuccessful.

21.3.4 Compounds with oxoanions

Because of the high ratio of ionic charge to radius, normal salts of Ti^{IV} cannot be prepared from aqueous solutions, which only yield basic, hydrolysed species. Even with Zr^{IV} and Hf^{IV}, normal salts such as $Zr(NO_3)_4.5H_2O$ and $Zr(SO_4)_2.4H_2O$ can only be isolated if the solution is sufficiently acidic, whilst basic salts and anionic complexes are readily obtained. Several oxometal(IV) compounds (i.e. "titanyl", "zirconyl") have been isolated but do not contain discrete MO^{2+} ions, being polymeric in the solid state. Thus, $TiOSO_4.H_2O$ contains chains of $-Ti-O-Ti-O-$ with each Ti being approximately octahedrally coordinated to 2 bridging oxygen atoms, 1 water molecule and an oxygen atom from each of 3 sulfates; $ZrO(NO_3)_2$ is also an oxygen-bridged chain, though hydroxy bridging, as in $ZrOCl_2.8H_2O$ mentioned above, is more common. By contrast, ion-exchange studies on aqueous solutions of Ti^{IV} in 2 M $HClO_4$ are consistent with the presence of monomeric doubly-charged cationic species rather than polymers, though it is not clear whether the predominent species is $[TiO]^{2+}$ or $[Ti(OH)_2]^{2+}$.

The anhydrous nitrates can be prepared by the action of N_2O_5 on MCl_4. $Ti(NO_3)_4$ is a white sublimable and highly reactive compound (mp 58°C) in which the bidentate nitrate ions are disposed tetrahedrally around the titanium which thereby attains a coordination number of 8 (Fig. 21.4). Infrared evidence suggests that $Zr(NO_3)_4$ is isostructural but hafnium nitrate
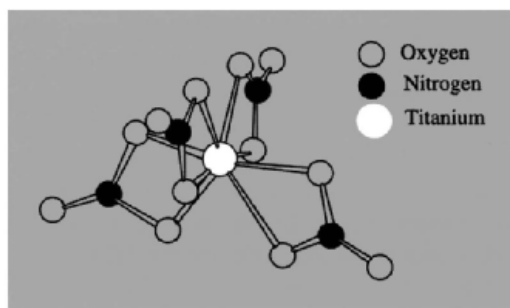

Figure 21.4 The molecular structure of $Ti(NO_3)_4$. Eight O atoms form a dodecahedron around the Ti and the 4 N atoms form a flattened tetrahedron.

[13] R. P. ZIEBARTH and J. D. CORBETT, *Acc. Chem. Res.* **22**, 256–62 (1989).
[14] F. A. COTTON, P. A. KIBALA and W. J. ROTH, *J. Am. Chem. Soc.* **110** 298–300 (1988).