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THE STRUCTURAL CHEMISTRY OF ZIRCONIUM COMPOUNDS

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A. INTRODUCTION

Many early studies of zirconium were of a practical nature involving mineral chemistry, metallurgy, analyses and related problems. Much of the information is recorded in patents. These aspects were thoroughly reviewed about ten or so years ago and the reader is referred to the relevant monograph or review[1-3].

Much of the basic chemistry of zirconium has appeared in the literature only during the past decade. A number of studies of zirconium in aqueous solution have recently appeared[4,5,12,13], as well as reviews on other aspects of the chemistry of zirconium[4-10]. By far the most comprehensive review on the chemistry of zirconium is that by Larsen[14]. It is also the most recent and covers the literature up to the beginning of 1969.

Successful research into the chemistry of zirconium has been pursued along two basic lines. These may be referred to as the "aqueous chemistry" and "non-aqueous chemistry" of the metal. Both have their difficulties. In aqueous solution zirconium compounds are readily hydrolysed from aquo species to hydroxy species to various polymeric species. In some studies these hydrolysed species have been identified, in others hydrolysis has been avoided by careful control of acidity. The non-aqueous studies are conducted in anhydrous solvents or salt melts. Difficulties arise in maintaining anhydrous conditions, but even more

TABLE 1

Molecular structures of zirconium compounds established by X-ray diffraction studies[a]

Compound	Geometry	Bond lengths (A)		Description	Footnotes	Ref.
Oxides						
ZrO_2	Seven-coordinate tetragonal-based trigonal-based polyhedral	Zr–O	2.04–2.26	Monoclinic	*b*	17–19
ZrO_2	Distorted dodecahedral	Zr–O	2.065, 2.655	Tetragonal	*c, d*	20
$BaZrO_3$	Octahedral	Zr–O	2.097	Perovskite structure		22
K_2ZrO_3	Square pyramidal	Zr–O bridging apical	 2.13 1.92	Anions are linked in chains of edge-sharing square pyramids with apices directed oppositely	*e*	23
ZrOS	Seven-coordinate complex polyhedral	Zr–O	2.13			24
Halides						
$ZrCl_4$	Tetrahedral			Vapour state	*f*	25, 26
$ZrCl_4$	Octahedral	Zr–Cl bridging apical Zr–Zr	 2.50 2.66 2.31 3.96	Octahedra are coupled by two edges to give a zig-zag chain	*g*	27
Cs_2ZrCl_6	Octahedral	Zr–Cl	2.44		*h*	28
$ZrBr_4$; ZrI_4	Octahedral			Coordination lattice with halide ions cubic close packed		29
β-$ZrCl_3$	Octahedral	Zr–Cl	2.55	Infinite linear chains of $ZrCl_6$ octahedra sharing opposite faces	*i*	31–33

α-ZrNCl	Tetrahedral			FeOCl-type structure	j	34
α-ZrNBr	Tetrahedral	Zr—N Zr—Br	2.12 2.85	FeOCl-type structure	j	34
β-ZrNCl	Distorted octahedral	Zr—N Zr—Cl	2.12 2.68	Hexagonal random sequence of ClZrNNZrCl	j, k	35
β-ZrNBr	Distorted octahedral	Zr—N Zr—Br	2.12 2.82	Hexagonal random sequence of BrZrNNZrBr	j, k	35
ZrNI	Tetrahedral	Zr—N Zr—I	2.16 2.95	FeOCl-type structure built up of layers comprising puckered sheets of N succeeded on either side by sheets of Zr and I	j	36
ZrF_4	Tetrahedral	Zr—F	1.94	Monomeric, vapour state	f	37
α-ZrF_4	Distorted square antiprismatic	Zr—F $\theta = 57°$	2.11	Antiprisms share corners to give three-dimensional array	l	38, 39
ZrF_43H_2O	Dodecahedral	Zr—F Zr—O	1.98—2.22 2.17—2.25	Dimeric with two dodecahedra sharing an *a* edge	m	43, 44
K_2ZrF_6	Dodecahedral	Zr—F $\theta_a = 35.3°$ $\theta_b = 74.6°$	2.18	Half the trapezoidal slant edges (*m*) are shared to give chains	n	47, 48
Rb_2ZrF_6	Distorted octahedral	Zr—F	2.04	Trigonal	o	49
γ-Na_2ZrF_6	Seven-coordinate irregular polyhedral with nine triangular faces	Zr—F	2.012—2.167	Each zirconium shares edges or corners with eight neighbouring sodium atoms	p	50
$(NH_4)_3ZrF_7$	Pentagonal bipyramidal	Zr—F	2.00—2.07	Disordered structure	q	51
$(N_2H_6)^{2+}ZrF_6^{2-}$	Eight-coordinate hendecahedral	Zr—F	2.12	Each prism shares edges with two neighbours giving infinite zig-zag chains (retaining C_{2v}), held together by cations via hydrogen bonds	ll	115
$Na_7Zr_6F_{31}$	Square antiprismatic	Zr—F	2.03—2.18	The extra F^- ion is in a cubic hole and disordered	r	53

TABLE 1 (continued)

Compound	Geometry	Bond lengths (A)		Description	Footnotes	Ref.
Halides (continued)						
$Na_5Zr_2F_{13}$	Face-centred trigonal prismatic	Zr–F	2.00–2.10	The face-centred fluoride bridges to give the dinuclear species		54
$Li_6BeF_4ZrF_8$	Dodecahedral	Zr–F $\theta_a = 43°$ $\theta_b = 65.5°$	2.05–2.16			55
$Cu(H_2O)_4 \cdot ZrF_6$	Octahedral				*s*	56
$[Cu(H_2O)_6]_2ZrF_8$	Square antiprismatic	Zr–F	2.08		*t*	56
$K_2Cu(H_2O)_6 \cdot Zr_2F_{12}$	Pentagonal bipyramidal	Zr–F	1.980–2.165	The anion is centrosymmetric and results from two distorted pentagonal bipyramids sharing an edge		57
$Cu(H_2O)_6 \cdot Cu_2(H_2O)_{10} \cdot Zr_2F_{14}$	Square antiprismatic	Zr–F terminal bridging	 2.06 2.18	Anion is dimeric with a double fluoride bridge		59
$Zr_7O_9F_{10}$	Both octahedral and pentagonal bipyramidal	Zr–X	1.98–2.46	O^{2-} and F^- are interchangeable		60
$Rb_5Zr_4F_{21}$	Octahedral, pentagonal bipyramidal, distorted square antiprismatic with one corner missing, and distorted square antiprismatic	Zr–F	1.90–2.24	Structure consists of cross-linked chains of Zr–F polyhedra		113
Sulphates						
α-$Zr(SO_4)_2$	Seven-coordinate tetragonal based trigonal based polyhedral	Zr–O	2.03–2.19	Each zirconium is linked to seven different sulphates; sulphates are bonded to either three or four zirconiums		61

γ-$Zr(SO_4)_2 \cdot H_2O$	Seven-coordinate tetragonal based trigonal based polyhedral	Zr–O	2.07–2.19	Zr is bonded to six bridging sulphates and one water molecule	*u*	62
α-$Zr(SO_4)_2 \cdot H_2O$	Seven-coordinate tetragonal based trigonal based polyhedral	Zr–O	2.07–2.22	Each zirconium is bound to five sulphates through either single or double oxygen bridges	*v*	64
$Zr(SO_4)_2 \cdot 4H_2O$	Square antiprismatic	Zr–O $\theta = 58°$	2.176, 2.183	$Zr(H_2O)_4{}^{4+}$ groups are bridged by sulphate ions giving a layered structure		65
α-$Zr_2(SO_4)_4(H_2O)_8 \cdot 2H_2O$	Dodecahedral	Zr–O	2.18–2.23	Alpha-pentahydrate; two sulphates are bridging, two are bidentate		66
β-$Zr_2(SO_4)_4(H_2O)_8 \cdot 2H_2O$	Dodecahedral	Zr–O	2.15–2.26	Beta-pentahydrate; same as alpha but with closer packing		67
$Zr_2(SO_4)_4(H_2O)_8 \cdot 6H_2O$	Dodecahedral	Zr–O	2.16–2.28	The heptahydrate; same as alpha but with additional water of crystallisation	*w*	68
$K_4Zr_2(SO_4)_6(H_2O)_4$	Dodecahedral	Zr–O	2.03–2.35	Two sulphates are chelating and two are bridging bidentate. All sulphates have two terminal oxygens. Similar to the three preceding structures		69
$Na_2Zr(SO_4)_3 3H_2O$	Dodecahedral	Zr–O	2.09–2.29	Similar to potassium salt above. Spirals of $[Zr(SO_4)_3(H_2O)_2{}^{2-}]_n$ held together by Na^+ ions	*kk*	116
$Zr(OH)_2SO_4$	Square antiprismatic	Zr–O	2.19	Infinite chains of $Zr(OH)_2{}^{2+}$ linked by sulphate ions	*x*	70, 71
$Zr_2(OH)_2(SO_4)_3 \cdot 4H_2O$	Dodecahedral	Zr–O	2.19	Sheets of $ZrSO_4{}^{2+}$ linked by double hydroxy bridges	*y*	70–72

TABLE 1 (continued)

Compound	Geometry	Bond lengths (A)		Description	Footnotes	Ref.
Hydroxy complexes						
$Zr_4(OH)_8(H_2O)_{16}Cl_8\cdot 12H_2O$	Dodecahedral	Zr–OH Zr–OH_2	2.142 2.272	Zirconyl chloride. Discrete cycles of four zirconiums linked by double hydroxy bridges	*z*	73, 74
$Zr(OH)_2(NO_3)_2(H_2O)_4$	Dodecahedral	Zr–O	2.22	Chains of $[Zr(OH)_2NO_3(H_2O)_2^+]_n$ joined by nitrate ions via hydrogen bonds		70
$Zr_4(OH)_6(CrO_4)_5\cdot 2H_2O$	Pentagonal bipyramidal	Zr–O	1.97, 2.17–2.21	Zig-zag chains of $[Zr_4(OH)_6CrO_4^{8+}]_n$ linked by OH^- and CrO_4^- ions		75
$(NH_4)_6Zr_2(OH)_2(CO_3)_6\cdot 4H_2O$	Distorted dodecahedral			Dimeric species with double OH bridges and bidentate carbonates		76
Inorganic salts						
$ZrSiO_4$	Distorted dodecahedral	Zr–O	2.15, 2.29	Two dodecahedra share an *a* edge	*aa*	77
$Zr(IO_3)_4$	Square antiprismatic	Zr–O $\theta = 58°$	2.197–2.216	Layered structure with Zr atoms linked by IO_3 bridges		78
ZrP_2O_7	Octahedral	Zr–O	2.018	Sodium chloride type lattice		79
α-$Zr(HPO_4)_2\cdot H_2O$	Octahedral	Zr–O	2.04–2.11	Each phosphate bonds to three different zirconiums giving a layered structure. Layers form Zeolitic-type cavities, each of which contains a water molecule		80

α-$Zr(HAsO_4)_2 \cdot H_2O$	Octahedral	Zr–O As–O	2.075 1.655	Isomorphous with the α-phosphate above		81
$ZrTe_3O_8$	Octahedral	Zr–O	2.01		*mm*	119
$Zr(BH_4)_4$	Twelve-coordinate truncated tetrahedral	Zr–B B–H	2.34 1.2	T_d symmetry	*bb*	82
Organic complexes						
$K_2Zr(NTA)_2 \cdot H_2O$	Dodecahedral	Zr–O Zr–N	2.18, 2.25 2.44	Monomeric anions. Ligand spans *a*, *m* and *g* edges	*m*, *cc*	84
$Na_4Zr(C_2O_4)_4 \cdot 3H_2O$	Dodecahedral	Zr–O $\theta_a = 35.2°$ $\theta_b = 73.5°$	2.23, 2.17	Monomeric anion. Ligands chelate along *m* edges	*m*	85
$ZrCl_4(diars)_2$	Dodecahedral	*dd*		Ligand chelates along *a* edges	*m*, *dd*	86
$Zr(N\text{-ethylsalicylaldiminato})_4$	Dodecahedral	Zr–O Zr–N $\theta_a = 36.85°$ $\theta_b = 69.46°$	2.055 2.539	S_4 symmetry. Ligand chelates along *g* edges	*m*	87
$Zr(cupferrate)_4$	Distorted dodecahedral	Zr–O	2.17–2.22	Monomeric species	*ee*	88
β-$Zr(acac)_4$	Square antiprismatic	Zr–O $\theta = 57.30°$	2.198	Ligand chelates along *s* edges	*m*, *ff*	89
$ZrCl(acac)_3$	Seven-coordinate distorted pentagonal bipyramidal	Zr–O Zr–Cl	2.08, 2.14 2.47	Monomeric	*ll*	117
$Zr\{\pi\text{-}(cp)Cl(acac)_2\}$	Dodecahedral	Zr–O Zr–Cl Zr–C	2.11, 2.20 2.50 2.55	π-cp occupies a trigonal face	*gg*	90, 91
$Zr\{\pi\text{-}(cp)(hfa)_3\}$	Pentagonal bipyramidal	Zr–O Zr–C	2.22 2.53	Five oxygen donors lie in a plane. The sixth oxygen and the π-cp occupy axial sites	*hh*	92, 93
$Zr\{\pi\text{-}(cp)_2Cl_2\}$	Distorted tetrahedral or wedge-shaped sandwich	Zr–Cl Zr–C Inter-ring angle 46°	2.309 2.522	Mononuclear in the vapour state		94

TABLE 1 (continued)

Compound	Geometry	Bond lengths (Å)	Description	Footnotes	Ref.
Organic complexes (continued)					
Zr[π-(cp)$_2$F$_2$]	Wedge-shaped sandwich	Zr–C 2.50 Zr–F 1.98 Inter-ring angle 52.2°			121
Zr[π-(cp)$_2$I$_2$]	Wedge-shaped sandwich	Zr–C 2.48 Zr–I 2.83 Inter-ring angle 54°			121
Zr[π-(cp)$_3\sigma$-cp]	Tetrahedral	σ Zr–C 2.47 π Zr–C 2.64 C–C 1.45			95, 96
Zr(benzyl)$_4$	Tetrahedral	Zr–C 2.27 Angle ZrCC 92°	Monomeric compound	*ii*	97

a Some of the information in this Table has appeared in other reviews[6–8,15,16].

b Monoclinic HfO_2 is isomorphous.

c Isostructural with red HgI_2.

d Cubic ZrO_2 has also been described[21] which has the fluorite structure with Zr–O = 2.20 Å. $ZrTiO_4$ has been described[120] as having a structure similar to columbite with Ti and Zr disordered.

e The apical oxygens are isolated and presumably doubly bonded to the zirconium atoms. K_2SnO_3 is isostructural.

f Electron diffraction study.

g Flat needles obtained by slow evaporation at 300° C. $ZrBr_4$, $HfCl_4$, $HfBr_4$ are isostructural.

h Rb_2ZrCl_6 is isostructural.

i Chloride ions are in a distorted hexagonal close-packed array with a third of the available octahedral holes occupied by zirconium atoms. $ZrBr_3$, ZrI_3, HfI_3 are isomorphous. Structures solved by powder methods. ZrF_3 possibly has a structure[30] similar to TaF_3 (ReO_3-type).

j X-ray powder study.

k High-temperature modification.

l HfF_4 (ref. 40), UF_4, CeF_4, NpF_4, ThF_4, PuF_4 are isomorphous. β-ZrF_4 is the same as monoclinic ZrF_4 (ref. 41) but its structure is not known[42].

m The edge nomenclature for the polyhedra is that defined by Hoard and Silverton[45] (see Fig. 2). $HfF_4 \cdot 3H_2O$ forms a polymeric chain[46], with the Hf in a distorted dodecahedral geometry.

n The compound is said to have *mm* symmetry. The Hf compound is isomorphous.

o Cs_2ZrF_6 is isomorphous.

p The γ-form is metastable below 460°C with respect to the Δ-form.

q This is a highly refined structure (R = 2.3%). A previous report[52] indicates that Cs_3ZrF_7 is isostructural.

r $NaUF_5$ is isomorphous.

s Ti structure solved. Zr and Hf compounds isomorphous.

t The copper ions have distorted octahedral geometry.

u An unrefined structure incorrectly assigned geometry as face-centred trigonal prismatic[63].

v The powder pattern of β-$Zr(SO_4)_2H_2O$ shows that the compound has very similar lattice parameters to the γ-form, with which it is probably isostructural[61,118].

w For the chemical inter-relationship of these last four sulphates see the text.

x Uranium and thorium compounds are isomorphous.

y Also described as isolated $Zr_2(OH)_2(H_2O)_4^{6+}$ joined by SO_4^{2-} bridges[66].

z Structure was originally described as square antiprismatic[69], but further refinement of new data[68] revealed D_{2d} symmetry and dodecahedral geometry. Zirconyl bromide, hafnyl chloride and bromide are isomorphous.

aa Similar to tetragonal ZrO_2.

bb Reflection data were collected at −160°C (R = 0.066). Electron diffraction studies[83] show that the tetrahedral configuration is retained in the vapour state, although there is considerable torsional motion about the Zr—B vector.

cc Hf complex is isomorphous. NTA ≡ nitrilotriacetate.

dd Ti structure investigated; V, Zr, Nb, Hf compounds all isomorphous. Ti–As = 2.71 A; Ti–Cl = 2.46 A; θ_a = 36.4°; θ_b = 72.5°. "diars" ≡ *o*-phenylenebis(dimethylarsine).

ee Cupferrate is the anion of *N*-nitroso-*N*-phenylhydroxylamine ($C_6H_6N_2O_2$).

ff Hf, Th, Pu complexes are isomorphous; acac ≡ acetylacetonate.

gg Also describable as distorted octahedral with Cl and π-cp *cis*. π-cp ≡ π-bonded cyclopentadienide.

hh hfa ≡ hexafluoroacetylacetonate.

ii Structure determined at −40°C. Benzyl is phenylmethyl (C_7H_7).

jj The metal geometry may also be described as a bi-capped trigonal prism with a mirror plane. It is sometimes referred to as distorted square-antiprismatic.

kk This compound is formed by slowly evaporating a solution of $Zr(SO_4)_2 4H_2O$ and Na_2SO_4 in a 1:1 molar ratio. The crystalline product is dried over P_2O_5.

ll The chloride group occupies one axial site. The pentagonal ring of oxygens is puckered because of steric effects.

mm Ti structure investigated. Zr, Hf, Sn compounds are shown to be isostructural by powder pattern studies.

limiting is the insolubility of initial products. Both lines of research have lead to large numbers of well-defined crystalline compounds or to species clearly identified in solution.

Stoichiometric arguments, when applied to the compounds of zirconium, have been singularly unsuccessful in predicting molecular structures and geometries. The reason for this lies in the ability of zirconium(IV) to assume a wide range of coordination numbers and geometries. Since speculative chemistry in such areas as reaction kinetics, synthesis, analysis, etc. depends on correct assumptions of the molecular geometries of compounds and intermediates, these aspects of zirconium chemistry remain unexplored.

But in the very recent past a large number of zirconium compounds have been subjected to diffraction studies for the elucidation of their crystal and molecular structures. It is only by basing further studies of zirconium firmly on such structural information that progress in this hitherto confused area of chemistry will be achieved.

B. MOLECULAR STRUCTURES OF ZIRCONIUM COMPOUNDS ESTABLISHED BY X-RAY DIFFRACTION AND RELATED TECHNIQUES

While it is true that that which crystallises out of solution is not necessarily the species which the solution contains, it is equally true that there must at least be a generic relationship between the two. It follows that a co-study of a solution and its solid derivatives is probably the soundest approach to solution chemistry. This review therefore tabulates all molecular structures of zirconium compounds which have been unambiguously established (Table 1). It is hoped that this will provide a sound basis for future work whether in the solid state or in solution.

C. APPLICATIONS OF TABLE 1

The way in which this compilation of structural information may be applied to solving problems in the chemistry of zirconium is best demonstrated in a series of examples.

(i) On the existence of the zirconyl group

On the question of the existence of the zirconyl group ($Zr{=}O^{2+}$) we conclude with Solovkin and Tsvetkova[11] that the species rarely occurs. This conclusion is based on the following arguments.

(1) Evidence based on empirical stoichiometry is totally unreliable; for instance, zirconyl chloride has the empirical formula $ZrOCl_2 \cdot 8H_2O$ but is in reality[98] $[Zr_4(OH)_8(H_2O)_{16}]Cl_8 \cdot 12H_2O$.

(2) Evidence based on infra-red spectra is vague and inconclusive. The metal—oxygen double bond is expected[99] to absorb strongly between 900 and 1100 cm^{-1} and the isolated oxygen bridge should absorb somewhat below 900 cm^{-1}. The oxygen in monoclinic zirconium dioxide[100] bridges several metal atoms and absorbs at 743 cm^{-1}. One would therefore expect the isolated Zr—O—Zr system to absorb at about 850 cm^{-1}. The oxyfluorides

all absorb in this region[6] with the exception of $ZrF_4 \cdot H_2O$, which has an intense absorption at 956 cm^{-1}. However, a band at 1642 cm^{-1} confirms the presence of water and the absence of the zirconyl group[6].

(3) These arguments apply equally well to the anhydrous compound whose empirical formula[101] is $ZrOCl_2$, which has an intense infra-red absorption centred at 877 cm^{-1}. This compound is formulated as containing a zirconyl group, but the identical compound obtained from the dehydration of "zirconyl" chloride octahydrate is presumed to contain tetrameric units linked by oxo bridges[102]. This latter formulation is consistent with the predictions of Clearfield[6].

(4) Table 1 shows that in compounds where the bond between zirconium and oxygen is a "single" bond the separation of these atoms can vary from 2.04 to 2.65 Å in the oxides [17-20], and 2.03 to 2.28 Å in the sulphates[64-71], 2.02 Å in the pyrophosphate[79] and 1.97 Å in the basic chromate[72]. It is difficult to predict the bond length which would unambiguously constitute a double bond between zirconium and oxygen.

In $BaZrO_3$ the shortest bond is 2.1 Å (ref. 22), while in K_2ZrO_3 it is 1.92 Å (ref. 23). This latter bond is to an isolated oxygen and in the opinion of this author constitutes the only probable example of a zirconium—oxygen double bond yet reported.

There is no doubt that the "zirconyl" group as a persistent species in solution is mythical.

The fact that zirconium(IV) prefers to form polymeric hydroxy-bridged species rather than zirconyl groups is not surprising in view of the large number of metals which behave similarly[103]. The explanation must lie in the essentially electrostatic character of the Zr—OH bond.

(ii) The nature of the sulphates of zirconium

The study of zirconium ions in aqueous sulphate media has received attention in several recent reviews[5,6,13]. There is, however, no clear indication in these studies of the identity of the zirconium species. A superficial study of the crystalline derivatives from such solutions seems to reveal a large number of different compounds whose inter-relationship is not immediately obvious.

X-ray crystal studies[61-72] of this series of sulphates and basic sulphates not only establishes the structure of each compound but enables their chemical inter-relationship to be convincingly rationalized.

Table 1 demonstrates how the various crystalline sulphates are structures. There are three zirconium environments: seven-coordinate tetragonal-based trigonal-based structure in the anhydrous sulphates and monohydrates; square antiprismatic in the tetrahydrate and the dihydroxy sulphate, and dodecahedral in all other structures. Sulphate ions are variously bidentate, bidentate bridging, tridentate bridging or quadridentate bridging.

The formation of these crystalline zirconium sulphates and their interconversions are controlled by vapour pressure and temperature. This inter-relationship is summarized in Fig. 1 which is based on a similar figure in ref. 66. The fact that these species can be so

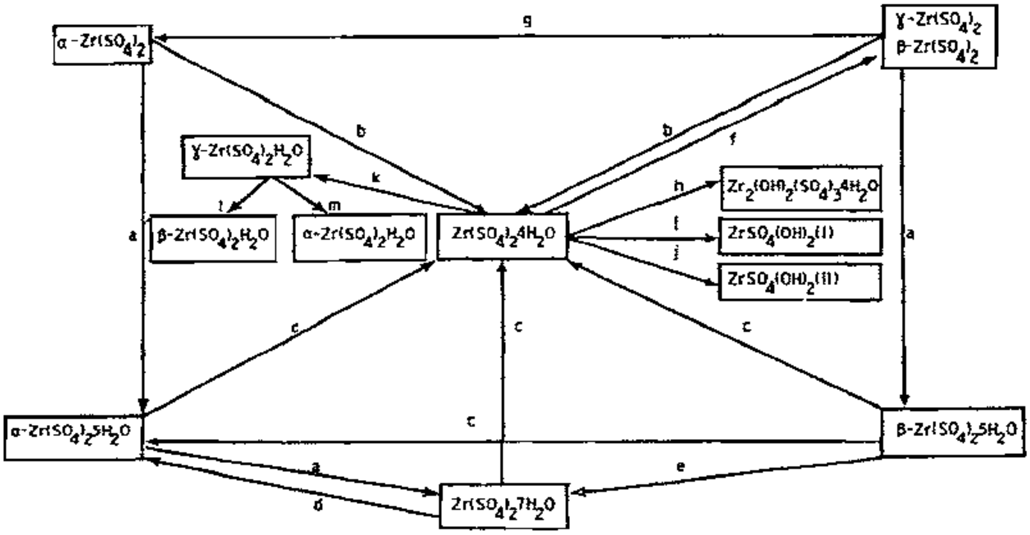


Fig. 1. Inter-relationship of the sulphates of zirconium. (a) Aqueous hydration; (b) vapour hydration, ambient conditions; (c) equilibration under controlled water vapour pressure; (d) dehydration under vacuum or over P_2O_5 at 0°C; (e) aqueous hydration at 0°C; (f) thermal decomposition; (g) equilibration with SO_3 or H_2SO_4 vapour; (h) neutral aqueous solution 100–150°C; (i) neutral aqueous solution 175–225°C; (j) neutral aqueous solution 250–300°C; (k) thermal decomposition at 200°C for one hour; (l) aging at room temperature; (m) equilibration over 75% H_2SO_4 at 155°C.

readily interconverted demonstrates that the sulphate ligand is very labile. Presumably the species present in the crystalline material is formed only during deposition. Complex ions in solution must be undergoing rapid exchange. Such lability is not incompatible with the high stability attributed to these species[6,13]. This excellent work has been the subject of a very recent review[118].

(iii) Structures of zirconium fluorides

Table 1 reveals that in its compounds with fluoride ions zirconium seems free to assume almost any coordination number and geometry[37–60]. Metal geometries include tetrahedral, octahedral, face-centred trigonal prismatic, pentagonal bipyramidal, square antiprismatic and dodecahedral as well as distorted octahedral, seven-coordinate irregular polyhedral, distorted square antiprismatic and distorted dodecahedral. Zirconium fluoride species may be monomeric, dimeric or polymeric. The stereochemistry seems to be determined by the counter-ions and the conditions existing during crystal formation.

In one compound, $Zr_7O_9F_{10}$, zirconium has both octahedral and pentagonal bipyramidal geometries and the oxides and fluorides are interchangeable[60]. In another compound, $Rb_5Zr_4F_{21}$, there are three coordination numbers and four geometries for zirconium – octahedral, pentagonal bipyramidal, distorted square antiprismatic with one corner missing and square antiprismatic[113].

TABLE 2

Geometric variations in zirconium compounds

Coordination number	Geometry
4	Tetrahedral
4	Distorted tetrahedral
5	Square pyramidal
6	Octahedral
6	Distorted octahedral
7	Pentagonal bipyramidal
7	Puckered pentagonal bipyramidal
7	Face-centred (or capped) trigonal prismatic
7	Tetragonal-based trigonal-based polyhedral
7	Distorted square antiprismatic with one corner missing
7	Seven-coordinate complex polyhedral with nine triangular faces
8	Dodecahedral
8	Square antiprismatic
8	Hendecahedral
8	Distorted dodecahedral
8	Distorted square antiprismatic
12	Truncated tetrahedral

The fluorides best illustrate the apparent lack of system in the stereochemistry of zirconium and emphasise the importance of direct structural studies in this field.

(iv) The stereochemistry of zirconium compounds

Table 1 demonstrates that zirconium may have coordination numbers of 4, 5, 6, 7, 8 or 12. Within this range of coordination numbers there are further geometric variations and these are summarised in Table 2.

The more regular geometries of the various coordination spheres around zirconium are depicted in Fig. 2. Although no compound of zirconium has yet been shown to be trigonal bipyramidal (five-coordinate) or trigonal prismatic (six-coordinate), these geometries have been included in Table 2 to support the stereochemical discussion and to emphasise the close inter-relationships of many of these geometries.

To overcome the inherent difficulty in the interpretation of two-dimensional representations of complex polyhedra, the coordination geometries are presented both as solid figures and as perspective skeletons. In each case the zirconium ion is presumed to be at the precise centre of the polyhedron with each apex occupied by the donor atom of a ligand. Conventional two-dimensional drawings are also given since these are most useful in schematic representations of complicated molecules. The labelling of some of the diagrams follows established literature practice[7,45].

From Fig. 2 it is possible to observe the close similarities between groups of geometries. Indeed the drawings have been oriented to emphasise these relationships. It is reasonable,

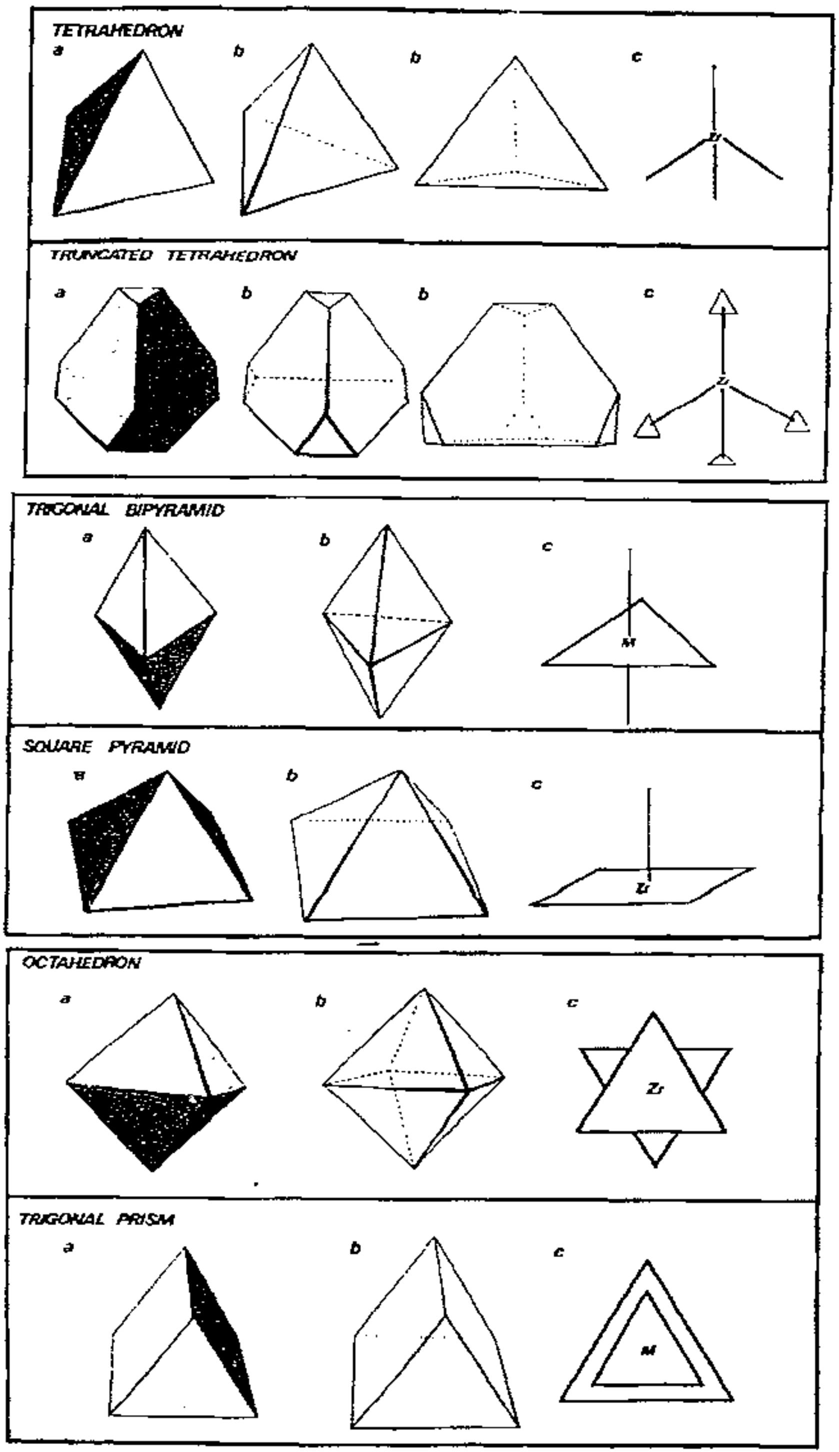
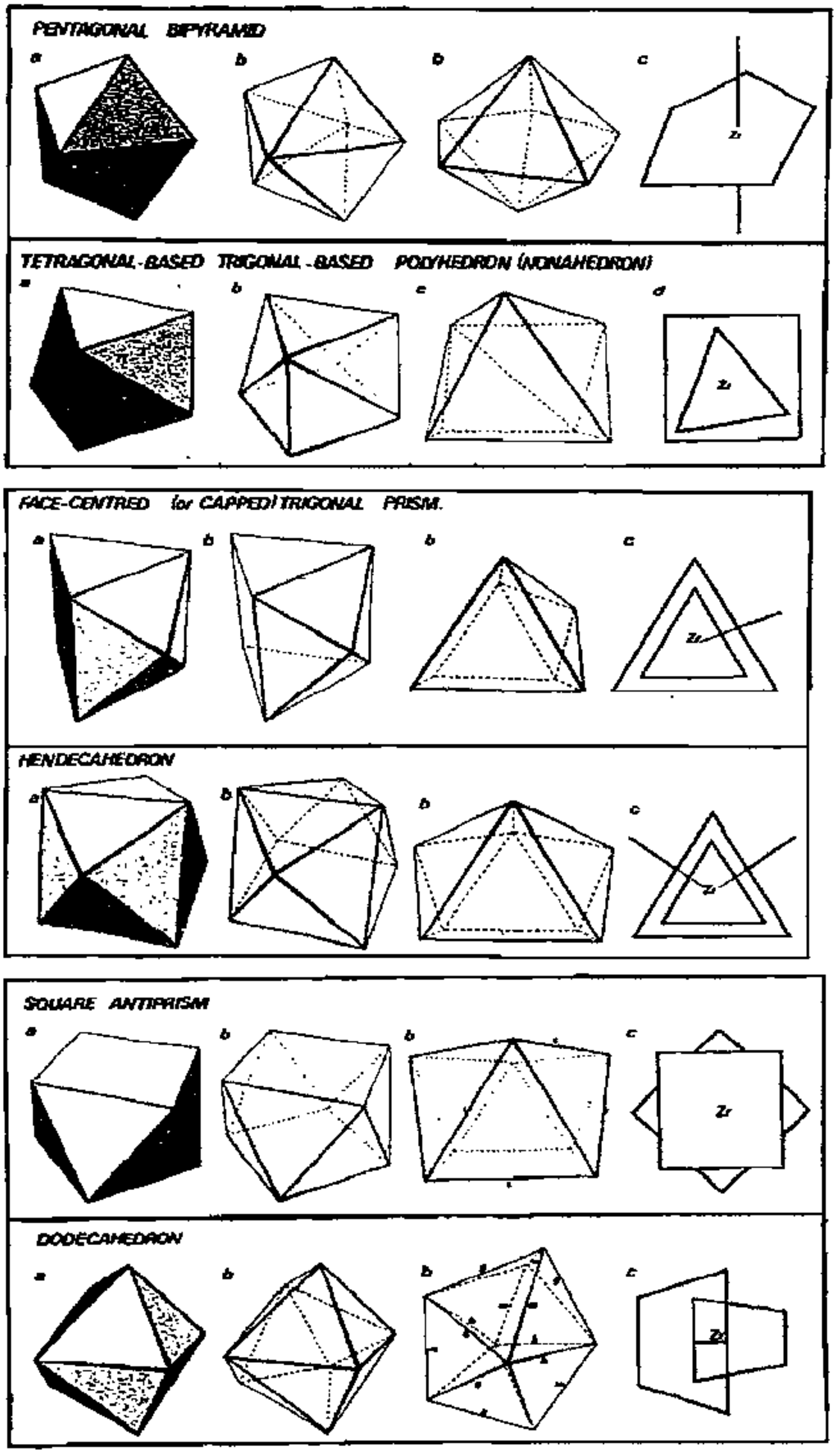


Fig. 2. Zirconium geometries and related polyhedra. (a) Solid



structure; (b) perspective skeleton; (c) formal representation.

in the case of zirconium, which can not only vary its geometry but also its coordination number with apparent ease, both to consider the variation of geometry for a given coordination number and also to trace the sequential relationship of geometries through a progressively expanding coordination number.

It is clear that the addition of one ligand to a square pyramidal compound gives the octahedral geometry, which upon a 60° internal rotation of opposite trigonal faces yields the trigonal prismatic arrangement. Addition of one ligand to this trigonal prism yields the face-centred, or capped, trigonal prism, and this, on a small movement of one face in conjunction with a shift of the cap into the plane of this face, yields the tetragonal-based trigonal-based polyhedron. The pentagonal bipyramid is formed from the capped trigonal prism by rotating the edge opposite the cap through 45° and moving the two apical points slightly. A smaller rotation of this edge yields the puckered pentagonal bipyramid. Thus the puckered pentagonal bipyramid may be regarded as either a distorted capped trigonal prism or a distorted tetragonal-based trigonal-based polyhedron.

Addition of one ligand to the capped trigonal prism yields the hendecahedron. Addition of one ligand to the tetragonal-based trigonal-based polyhedron together with a slight twist of one face yields the square antiprism. Folding of one square face of the square antiprism about a diagonal yields the hendecahedron. Folding the square face of the hendecahedron about a diagonal yields the dodecahedron. Obviously both a distorted dodecahedron and a distorted square antiprism may be equally well described as distorted hendecahedra.

It thus appears that for low coordination numbers the interconversion of one regular geometry to another is a major stereochemical event, but for higher coordination numbers, especially 7 and 8, there is a greater variety of possible geometries with relatively much slighter movement of ligands required to achieve a transition from one to the other. This apparent low energy of geometric interconversion may contribute to the variety of geometries exhibited by zirconium in compounds wherein the metal has seven or eight nearest neighbours.

In fact the geometry of zirconium in its compounds appears to be determined by the nature of the donor atoms, the charge on the ligand, the stoichiometry of reactants in the preparative process, the size and chelating ability of ligands, vapour pressure, temperature and other physical characteristics during crystal formation. The bonding orbitals of the metal show little preference for a specific geometry.

The lability of all zirconium(IV) species, with the exception of cyclopentadienyls, is probably associated with this ability of zirconium to assume a variety of geometries and to change easily from one geometry to another. Hence there is little likelihood of success in studying the molecular geometries of zirconium species by the classical methods of isomer separation.

On the other hand, zirconium provides an excellent opportunity for the study of geometric variations about a metal. The stereochemical requirements of multidentate ligands should dictate the geometries of their zirconium complexes, and steric interactions of various conformations in such complexes might be observed in the actual variation of the metal geometry.

Finally it should be pointed out that while the great majority of information on the geometry of zirconium compounds comes from diffraction studies, the careful application of NMR spectroscopy has already proved successful[114] in confirming the stereochemistry[90,91] of $Zr[\pi\text{-cpCl(acac)}_2]$ and in tracing its geometric interconversions in solution. It is anticipated that many similar studies will link the molecular geometries of zirconium compounds determined by diffraction studies with equivalent species in solution.

(v) The nature of bonding in zirconium compounds

Assuming the following ionic radii: Zr^{4+}, 0.79 Å; Cl^-, 1.81 Å; F^-, 1.33 Å; O^{2-}, 1.32 Å, and O^-, 1.76 Å, then Table 1 reveals that the observation[104] that in zirconium acetylacetonates "the bond lengths are given by the sum of the ionic radii" is generally true.

Calculations[45,105–107] show that energies of the alternative geometries for eight-coordination are not very different. Indeed it has been possible to rationalise the bonding for square antiprismatic zirconium(IV) in zirconyl chloride[108], even though a subsequent study[72] has shown that the metal is actually in a dodecahedral environment.

Not only has no set of isomers for any compound of zirconium(IV) ever been separated into its component isomers[8], but highly stable complexes such as $Zr(acac)_4$ (refs. 109, 110) and $[Zr(C_2O_4)_4]^{4-}$ (refs. 111, 112) have been shown to be very labile.

All these observations are consistent with a zirconium ion of small radius and high charge, which is essentially spherical, and whose attraction for anions or dipoles is essentially electrostatic. The Zr^{4+} ion has already achieved a noble gas structure and there is no ligand-field stabilization of bonding orbitals.

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