The Heavy Transition Elements

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THE HEAVY TRANSITION ELEMENTS

A Macmillan Chemistry Text

Consulting Editor: Dr Peter Sykes, University of Cambridge

COMPLEXES AND FIRST-ROW TRANSITION ELEMENTS: David Nicholls

Preface

The study of transition metals and their compounds occupies a prominent place in most first-degree chemistry courses. In many cases considerable attention is paid to the first-row transition series, much less attention to the second- and third-row metals, while the lanthanides and actinides are treated with the utmost brevity. The origin of this imbalance is probably to be found in a combination of two factors. The first is that the industrially important, well-known and abundant transition metals are the 3d metals such as copper, iron and nickel. Secondly, the quantitative aspects of ligand-field theory are more readily applied to the 3d metals than to the 4d, 5d, 4f and 5f metals because of the relative magnitudes of the physical parameters, such as the spin–orbit coupling constant and the crystal-field splitting parameter, that are involved.

This book, which is a sequel to a cognate volume† dealing with the 3d metals, gives an account of the 4d, 5d, 4f and 5f metals, which it is hoped will be adequate for any first-degree requirements and for postgraduate courses dealing with general aspects of transition-metal chemistry. The treatment is given in sufficient range and detail to allow considerable latitude to the course organiser and student in their choice of precise topic and level of approach. We have not hesitated to include a high proportion of descriptive chemistry, in the conviction that a sound knowledge of experimental facts forms the basis of any scientific discipline. This style of treatment may also be useful to research workers requiring a general view of some particular area of 4d, 5d, 4f and 5f chemistry; it is not intended, however, to provide a detailed introduction to research.

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† *Complexes and First-Row Transition Elements,* by David Nicholls

Abbreviations for Common Ligands

acac	acetylacetone anion
bipy	2,2′-bipyridyl
bzac	benzoylacetone anion
cp	cyclopentadienyl anion
diars	*o*-phenylenebisdimethylarsine
diglyme	2,2′-dimethoxydiethylether
diphos	1,2-diphenylphosphinoethane
dma	N,N-dimethylacetamide
dtpa	diethylenetriaminepenta-acetic acid anion
EDTA	ethylenediaminetetra-acetic acid anion
hal	halogen anion
hfac	hexafluoroacetylacetone anion
nta	nitrilotriacetic acid anion
oxine	8-hydroxyquinoline anion
phen	1,10-phenanthroline
py	pyridine
THF	tetrahydrofuran

Contents

TITANIUM

Metal: h.c.p.; m.p. 1680°; I_1 : 6.83 eV; I_2 : 13.57 eV; I_3 : 27.47 eV
Oxides: TiO, Ti_2O_3, TiO_2
Halides: TiX_2 (X = Cl, Br, I), TiX_3 and TiX_4 (X = F, Cl, Br, I)

	Oxidation State and Representative Compounds				
	0	1	2	3	4
Typical donor atom/group			Hal	O,Hal,N	O,Hal,N,As,etc.
Co-ordination number					
3				√ $Ti\{N(SiMe_3)_2\}_3$	
4 tet					√√ $TiCl_4$
5 T.B.P.				√√ $TiBr_3(Me_3N)_2$	√ $TiOCl_2(Me_3N)_2$
5 S.P.					?
6	√† $Ti(bipy)_3$		√√ $TiCl_2$	√√√ $[Ti(urea)_6]^{3+}$	√√√ $TiCl_4(Cl_3PO)_2$
7					√ $TiCl(S_2CNMe_2)_3$
8					√ $TiCl_4(diars)_2$

† 'Suspect' ligand; ? Suspected; √ Known; √√ Several examples; √√√ Very common

1 Zirconium and Hafnium

The three pairs of metals Y, Lu; Zr, Hf; Nb, Ta show a striking resemblance between the lighter and the heavier metal of each pair, arising from the predominant stability of the highest, or group, oxidation state, together with the ionic nature of the bonding and the close similarity of ionic radii. Thus both zirconium and hafnium are rather poorly represented in oxidation states other than +4, and the ionic radii are Zr^{4+} = 74 pm and Hf^{4+} = 75 pm, leading to chemical properties that differ only in comparatively minor respects. However, hafnium has been investigated to a smaller extent than has zirconium, so the factual basis for the statement that their properties are similar is less complete than might be desirable. The chemistry is relatively straightforward, being mainly that of the 4+ ions. Since these are fairly large, high co-ordination numbers are frequent. There are no known carbonyls but numbers of σ- and π- bonded organometallics have been prepared.

The metals occur as zircon, $ZrSiO_4$, and baddeleyite, a form of ZrO_2. As would be expected on account of their similar properties, they always occur together but hafnium is much less abundant than zirconium and only one zirconium atom in fifty is on average isomorphously replaced by hafnium.

1.1 The Metals and their Aqueous Chemistry

Zirconium metal was isolated by Berzelius in 1824 by potassium reduction of a fluoride. Hafnium was not obtained until 1923, a lengthy fractional crystallisation of complex fluorides (as with niobium and tantalum) being necessary before the pure hafnium complex could be reduced with sodium. The hafnium had remained undetected by ordinary chemical methods and its presence was first demonstrated by X-ray spectroscopy.

Either metal is now prepared by reduction of the tetrahalide vapour.

$$ZrCl_4 + 2Mg \xrightarrow[Ar]{1150^\circ} 2MgCl_2 + Zr$$

Excess Mg and $MgCl_2$ are removed by vacuum distillation; if necessary, the product may then be zone refined.

Both metals are high melting, having m.p.s 1852° (Zr) and 2150° (Hf). They have the hexagonal close-packed structure at ordinary temperatures. Zirconium metal is resistant to corrosion by air, most cold acids, and alkalis, but is attacked by hot aqua regia or hydrofluoric acid. Since it also has a low neutron absorption cross-section (weighted average of five isotopes, 0.18 barns†) it may be used for atomic-pile construction. Hafnium must be absent, however, since its average (six isotopes) is 105 barns. This separation is achieved by ion-exchange chromatography or by solvent extraction with tributylphosphate in ways essentially similar to those used for separations within the lanthanide and actinide series. The separation is, of course, carried out before preparation of the tetrahalide and reduction to the metal. Zirconium–niobium alloys are useful superconductors.

Because of hydrolysis, the hydrated ions $[M(H_2O)_x]^{4+}$ apparently do not exist in solution. Hydrous zirconium and hafnium oxides are soluble in aqueous HF, HCl, H_2SO_4 and HNO_3. Unlike the neighbouring metals, Nb and Ta, which form MO^{3+}, there is no evidence for ZrO^{2+} or HfO^{2+}. Thus an X-ray analysis of the compound $ZrOCl_2.8H_2O$, obtained from dilute hydrochloric acid solution, shows that it contains the polymeric cation $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$. The Zr—(OH)—Zr

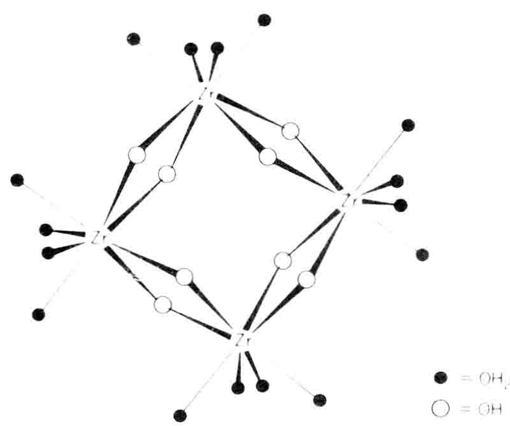

Figure 1.1 The tetrameric $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$ cation found in $ZrOCl_2.8H_2O$ (after T. C. W. Mak, *Can. J. Chem.*, **46** (1968), 3491)

bridges and the eight-co-ordination, dodecahedral in this case, are as expected for a moderately large cation with a rather high charge number (see figure 1.1). It is uncertain whether this species predominates in aqueous solution; the degree of polymerisation is pH dependent, increasing with rise of pH. There is some evidence that a trimeric species is present in 2.8 M HCl. There is no true hydroxide, hydrated forms $Zr(OH)_4(H_2O)_x$ being obtained.

The fluoride and sulphate anions have greater affinities for Zr^{4+} than has Cl^- and uncharged or anionic species are readily formed at fairly low acid concentrations. Thus the hydrated sulphate $Zr(SO_4)_2.4H_2O$ crystallises from 6 M H_2SO_4; the structure involves square antiprismatic co-ordination of zirconium. Fluoro-complexes include $Zr_2F_8.6H_2O$ (dodecahedral co-ordination—see figure 1.2a) and $HfF_4(H_2O)_2.H_2O$ (square antiprism with four bridging fluorines—see figure 1.2b).

† 1 barn = 10^{-28} m^2

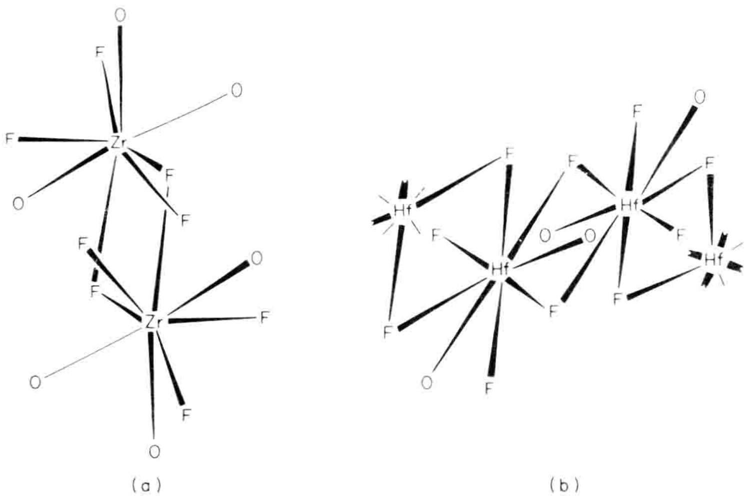

Figure 1.2 (a) The dimeric structure of $ZrF_4.3H_2O$; (b) the polymeric structure of $HfF_4.3H_2O$ (after D. Hall, C. E. F. Rickards and T. N. Waters, *Chem. Ind.* (1964), 713; *Nature, Lond.*, **207** (1965), 405)

Other salts of interest include the complex hydrated oxalate $Na_4[Zr(C_2O_4)_4].3H_2O$, which has dodecahedral co-ordination, and the hydrated nitrate $Zr(NO_3)_4.5H_2O$, obtained from cold concentrated nitric acid. The unsolvated nitrate $Zr(NO_3)_4$ may be obtained by

$$ZrCl_4 + 4N_2O_5 \rightarrow Zr(NO_3)_4 + 4NO_2Cl$$

It is volatile and the zirconium is doubtless eight-co-ordinated in a dodecahedral manner with bidentate nitrate groups; there is some spectroscopic evidence (infrared and Raman) for this. The hafnium compound firmly holds on to a molecule of N_2O_5 as $Hf(NO_3)_4.N_2O_5$.

1.2 Oxides

Apart from a volatile unstable species, probably the monoxide, formed by heating zirconium-zirconium dioxide mixtures, the dioxides are the only oxides. At ordinary temperatures, monoclinic forms with irregular seven-co-ordination are stable; at very high temperatures the fluorite structure is adopted. The dioxides may be obtained by heating the hydrated hydroxides. Zirconium dioxide, being a rather inert substance after strong ignition (for example, it is then unattacked by hot aqueous HF) and being stable up to over 2000°, forms a useful refractory material and ceramic opacifier or insulator. For these purposes, addition of a little CaO gives a stable fluorite structure, thus avoiding the adverse mechanical consequences of phase changes on repeated heating and cooling.