THE HEAVY TRANSITION ELEMENTS

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COMPLEXES AND FIRST-ROW TRANSITION ELEMENTS: David Nicholls

The Heavy Transition Elements

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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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S. A. Cotton
F. A. Hart

[†] *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	<i>o</i> -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

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, Ti₂O₃, TiO₂
 Halides: TiX₂ (X = Cl, Br, I), TiX₃ and TiX₄ (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				$\sqrt{\text{Ti}\{\text{N}(\text{SiMe}_3)_2\}_3}$	
4 tet					$\sqrt{\text{TiCl}_4}$
5 T.B.P.				$\sqrt{\text{TiBr}_3(\text{Me}_3\text{N})_2}$	$\sqrt{\text{TiOCl}_2(\text{Me}_3\text{N})_2}$
5 S.P.					?
6	$\sqrt{\dagger}$ Ti(bipy) ₃		$\sqrt{\text{TiCl}_2}$	$\sqrt{\text{Ti}\{\text{urea}\}_6]^{3+}}$	$\sqrt{\text{TiCl}_4(\text{Cl}_3\text{PO})_2}$
7					$\sqrt{\text{TiCl}(\text{S}_2\text{CNMe}_2)_3}$
8					$\sqrt{\text{TiCl}_4(\text{diars})_2}$

† 'Suspect' ligand; ? Suspected; $\sqrt{\text{Known}}$; $\sqrt{\text{Several examples}}$; $\sqrt{\text{Very common}}$