

Oxidation States of Ruthenium and Osmium

COMPREHENSIVE COORDINATION CHEMISTRY II. FROM BIOLOGY TO NANOTECHNOLOGY

Volume 5 TRANSITION METAL GROUPS 7 AND 8

EDITED BY E. C. CONSTABLE AND J. R. DILWORTH; EDITORS-IN-CHIEF, JON A. McCLEVERTY AND THOMAS J. MEYER, Elsevier, Amsterdam, 2003, 876 pages, ISBN 0-08-0443273 (Volume 5); ISBN 0-08-0437486 (Set), U.S. \$ 5975, € 6274 per Set

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Volume 5 in the book set "Comprehensive Coordination Chemistry II" (CCCII) presents a survey of important developments in the chemistry of the transition metals of Groups 7 and 8: manganese, technetium, rhenium, iron, ruthenium (Ru) and osmium (Os), published from 1982 to 2002. Volumes 6 and 9 in this 10 book set, covering work on the other platinum group metals have been previously reviewed (1, 2). In Volume 5, the material for each element is organised by oxidation state of the metal and also by the nature of the ligands involved, with additional sections covering special features of the coordination chemistry and applications of the complexes. However, only the oxidation states of ruthenium and osmium are reviewed here.

Low Oxidation States

In Chapter 5.5 entitled 'Ruthenium and osmium: low oxidation states' by Catherine E. Housecroft, the low oxidation states of ruthenium and osmium are covered. Relatively little work has been done for the 0 and +III oxidation states since the earlier volume, published in 1987, in contrast to the large amount of work on the +II oxidation state. The chemistry of the 0 oxidation state is largely organometallic, and this is dealt with in the companion series: "Comprehensive Organometallic Chemistry".

Much of the work on the +II state is due to the interesting photochemical properties of, in particular, ruthenium bearing heterocyclic nitrogen ligands. Such complexes have been studied for the photoreduction of water and used as sensitising dyes in photochemical cells with similar levels of performance to silicon cells. The section is domi-

nated by the chemistry of complexes containing the bipyridine (bpy) ligand.

Many complex ligands designed to extend the conjugation of the aromatic system or otherwise modify the electronic properties of the complex, have been prepared. The complexes can be simple mononuclear species, such as $[\text{Ru}(\text{bpy})_3]^{2+}$, dinuclear $[(\text{bpy})_2\text{Ru}(\mu\text{-L})\text{Ru}(\text{bpy})_2]^{n+}$ or polynuclear.

High Oxidation States

The high oxidation states of ruthenium and osmium are areas that are generally only very lightly covered by most chemistry reference books, even those that are dedicated to the chemistry of platinum group metals and catalysis. Happily in this 2nd edition of "Comprehensive Coordination Chemistry" this matter is very much set right. In Chapter 5.6 on 'Ruthenium and osmium: high oxidation states' by Chi-Ming Che and Tai-Chu Lau, the VIII to IV oxidation states receive over 100 pages and more than 600 references detailing all the work that has been published in this area from 1982 to 2002.

The structure of the review is clear and concise with separate sections for all the five high oxidation states covered. Inside each of these sections complexes are classified according to the ligands involved, covered so that one finds nitrogen-ligated complexes first, then oxo complexes, followed by sulfur, halide, hydride and finally any miscellaneous ligands not already covered. This enables the reader to use the review as a quick and powerful reference tool to find out about a specific area of interest.

Sensibly the authors begin their review of the literature in this area by looking at Ru(VIII) and

Os(VIII) as it is from here that many of the VII to IV complexes are prepared. Although not very much new material is covered for ruthenium, the catalytic properties of osmium tetroxide are covered in some depth particularly the dihydroxylation of and aminohydroxylation of alkenes. Several new osmium oxo halo complexes are also included and references are given for their synthesis routes and X-ray structures.

The main area covered in the VII oxidation state is the use of perruthenate as a selective oxidant for the conversion of alcohols to aldehydes or ketones with a variety of co-oxidants, but $[\text{OsO}_4]^-$ is also mentioned even though relatively little work has been published on this system.

By the time we reach the Ru(VI) and Os(VI) section the amount of material covered becomes too great to be covered in this short review. Not surprisingly the majority of the chemistry here involves multiple metal-ligand bonds particularly the nitrodo complexes, and a wealth of spectroscopic and X-ray data and references are supplied to support the earlier literature.

The Ru(VI) and Os(VI) polypyridyl and oxo complexes almost deserve a book in their own right, but all the key areas are covered in this subsection including the electrochemistry of these complexes, their IR spectra and X-ray structures, not forgetting their use as oxidants of both organic and inorganic substrates – complete with kinetic data!

Compared to the (VI) oxidation state section, the (V) oxidation state section at first appears to be rather frugal, but it soon becomes clear that this is as a result of the instability of many of these systems. Despite this there is still plenty of structural, spectroscopic and electrochemical data for these complexes.

Finally we come to the large (IV) oxidation state section where once again the nitrogen- and oxygen-based ligands dominate. As expected by now, the chemistry, spectroscopy and structures of these complexes are all covered in detail and sufficient references are supplied so that anyone starting to work in this area would rapidly become proficient.

Overall the authors are to be congratulated on their review of this specialist area. The wealth of

synthetic, spectroscopic and electrochemical information it contains make this an absolutely vital reference for anyone working with Ru or Os in their VIII to IV oxidation states, or for those working with their low oxidation states.

References

- 1 A. K. Keep, *Platinum Metals Rev.*, 2004, 48, (2), 64
- 2 J. M. Fisher, R. J. Potter and C. F. J. Barnard, *Platinum Metals Rev.*, 2004, 48, (3), 101

The Reviewers



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