Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Organometallic Chemistry 689 (2004) 2733–2742
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Book review

Comprehensive Coordination Chemistry II
From Biology to Nanotechnology
J.A. McCleverty, T.J. Meyer (editors in-chief); Elsevier, Amsterdam, 2003, 10 volumes, 9500 pages, ISBN 0-08-043748-6, Eur 6274.00 (US$5975.00)

An updated version of the original Comprehensive Coordination Chemistry I (*CCCI*) that appeared in 1987 is to be welcomed. This is rather an unusual publication to review, in that it is clearly impossible for any one individual to read critically all 9500 pages. For that reason I have asked my distinguished colleagues in the Chemistry Department of the University of Sussex to review individual volumes, and their accounts are presented below. Finally, I have attempted to provide a summary of our combined views. No attempt has been made to impose a single style of presentation on the individual reviews. Here I would add only three comments. The first is that an electronic version of Comprehensive Coordination Chemistry II is also available. The second is that the organisation of the volumes is not necessarily the same as was advertised in the earlier prospectus, but the arrangement described here corresponds to the actual volumes. The third is that at the current rate of Euro/US$ conversion, the quoted dollar price looks to be a real bargain! However, the publisher states that the prices are subject to change, so it is advisable to check before ordering.

Volume 1. Fundamentals: ligands, complexes, synthesis, purification and structure, volume editor A.B.P. Lever

This is the first of two volumes of Comprehensive Coordination Chemistry II (*CCCII*) that, rather than focusing on a specific area of the Periodic Table or application of coordination compounds themselves, deals with more general themes within the subject. Clearly from the breadth of the subject matter that could be included under the title, the collection of material is unable to satisfy all readers and there will always be individuals who feel that certain key areas have been omitted. However, for the purposes of this evaluation, rather than dwell on any material that has not been included, the editors' opinion concerning which topics should be included has been respected, and the following review concerns the material presented within the volume.

The main text has been divided up into five sections. The first is by far the largest (over half of the contents of this volume) and is given the simple and yet daunting title, "Ligands". Of necessity this chapter is further divided (into twenty four subsections) that focus mainly on particular ligand families or groups, such as bipyridines, Schiff base ligands, and polypyrazolylborate and scorpionate ligands. Scattered amongst these ligand-specific sections are more general reviews of ligand *types* including discussions of polyatomic bridging ligands and higher denticity ligands. As far as possible, the general approach appears to have been to organise the different sections together with respect to the atom that upon coordination interacts with the metal ion. As such, a number of nitrogen-based ligands are initially discussed, followed by sections on ligands containing the heavier pnictides and the chalcogens. The final three sections deal somewhat briefly with three established classes of ligand, namely calixarenes, porphyrins and phthalocyanines.

Generally, each section deals with the preparation and properties of the ligands to a greater extent than the coordination chemistry, which is presumably examined in more detail in subsequent volumes that are organised by metal Periodic Groups. An extremely high standard of presentation is maintained throughout this chapter and the diagrams very clearly indicate the (often complicated) interactions between multi(hapto) ligands and the metal centre. Particular mention should be made of the section on 1,2-diazine ligands which, in the true vein of a text concentrating on coordination chemistry, illustrates different observed bonding modes with clear ORTEP representations of examples, taken primarily from the authors' own work in the area. Because it avoids hardcore organic chemistry, this section will be of use to a reader who wishes to know about general synthetic approaches to different ligand types without going into too much detail. The up-to-date references should provide access to further information as required.

The second section of this volume is entitled "Synthesis, Purification, and Characterisation of Coordination Compounds", again a rather lofty title which, on the face of it, encompasses all of the quintessential aspects

doi:10.1016/j.jorganchem.2004.05.003

of our discipline. The first topic in this section deals with aqua complexes of the metallic elements. A brief introduction is followed by a survey of the types of metal aqua ion that form organised by Groups of the Periodic Table. Basic structural features such as the coordination number and the geometry of the hydrates are described. The remainder of this topic is examined in terms of the dynamic ligand-substitution processes that occur with these species. Initially this subject is dealt with in a general fashion that provides a useful background text for these processes and how they are measured, before specific elements are looked at in more detail. The remaining three sections deal with solvents and ionic liquids, chromatographic methods and crystal growth methods. The brevity of these discussions would do little more than whet the appetite of anyone with a genuine interest in these areas, although for newcomers or students/graduates who may be unfamiliar with these subjects they do provide some useful basic information and are well referenced to up-to-date developments.

Section 3, ''Reactions of Coordinated Ligands'', opens with a general introduction that considers the factors affecting reactivity and the types of reaction that can occur. This is a general treatment and again may be of use to students who wish to gain basic knowledge in the area. The remainder of the section looks in turn at the structures and reactivities of complexes containing carbon dioxide, nitric and nitrous oxide, dioxygen, oximes and nitriles. These topics are dealt with in varying amounts of detail, from a rounded discussion of NO/N_2O complexes that addresses synthesis, structure, bonding and characteristic reactions to a woefully inadequate (four pages!) glance at dioxygen complexes.

The next Section, entitled ''Stereochemistry, Structure and Crystal Engineering'', jumps in with some theoretical assessments of lone-pair effects and outer-sphere coordination. To appreciate fully these discussions some prior knowledge is essential and, while of interest to specialists in the field, they will be of limited use to the more general coordination chemist. This section is rounded off with a brief report on solid state, crystal engineering and hydrogen bonds. While merely scratching the surface of this extensive field of research, this text manages to do so in a well-organised fashion that looks at strategies that are employed in the development of 2D- and 3D-architectures, with some nice examples gleaned from the recent literature.

The final section in this volume concerns ''New Synthetic Methods'' and is timely. Some of the more exotic techniques that have been developed over the past few years are described (e.g., sonochemistry) although some of the topics are better described as 'preparations' rather than synthetic methods (e.g., spectroelectrochemistry). Generally each technique is described in basic terms and subsequently expounded upon with illustrative examples from the current literature. One curious minor detail is that the colour plates associated with the sections on solid state methods, hydrothermal and sol–gel have actually been inserted some 300 pages earlier in the middle of one of the discussions concerning ligands. Presumably this is due to some technical production issues, but it does mean one has to flick back and forth to benefit from these illustrations. As a real reflection of the diverse interests of chemists in the area of coordination chemistry and truly bringing home the vast field over which this subject is able to cast its canopy, the final section of this volume deals with applications of genetic engineering. Whilst anyone with a true interest in this area will likely find much more useful and in-depth texts elsewhere, the inclusion of this section reflects the realisation that, to be of value to modern coordination chemists, texts such as these can no longer exist as a list of metal–ligand complexes.

To summarise, owing to the wide range of topics covered, this text will probably not be of use in its entirety to any one individual. It does however serve as a useful starting point for someone who wishes to know more about a particular facet of coordination chemistry, and will provide useful background knowledge to students and researchers alike.

M.P. Copes

Volume 2. Physical methods, theoretical analysis, and case studies, volume editor A.B.P. Lever

In his introduction to this volume, the editor, a distinguished spectroscopist, states that his intention in the first two volumes of *CCCII* has been to lay down the fundamentals of coordination chemistry, as they are understood in the early part of the twenty-first century. The volume has been assessed on the basis of estimating how far this aim has been fulfilled.

The contents of this volume are divided into four sections. The first, ''Physical Methods'', comprises more than half the book, and is principally an account of various spectroscopies, plus sections on gas-phase coordination chemistry, diffraction methods, electrochemistry and magnetism. The second section is called ''Theoretical Models, Computational Methods, and Simulation''. The third very short section is called ''Software'', and the final section is concerned with ''Case Studies''.

This volume will probably be very useful for anyone wishing to spend time browsing through it to get a general idea of the techniques discussed. However, it is difficult to imagine anyone deciding that this will be the first choice of a source to obtain more specific information. For example, the NMR treatment starts with the intention of emphasising those aspects developed since 1990, which necessarily means that there are significant

omissions. It discusses briefly solution measurements of less-sensitive nuclei, chemical shifts, and coupling constants but also recommends the classic book by Harris as a primary reference. It deals quickly with structure determinations and dynamics, mentioning some selected pulse sequences, and then moves on to special topics, high-pressure studies and relaxation measurements. Diffusion measurements get a short treatment, and then solid-state measurements and finally the characteristics of selected ligand nuclei are summarised. All this is done in some 25 pages, but there follows an enormous list of 537 references. This section will undoubtedly prove a good starting point for anyone wanting to know what was the state of the art at the time of writing, but it would not tell you very much about how to do things. However, the treatment throughout the volume is uneven. Simple EPR is dealt with more superficially in about 10 pages, with 37 references, though double resonance and spin-echo techniques are given further consideration. This is indeed really a summary of what is achievable rather than a guide to how to do it.

The treatment of electrochemistry is rather different. It begins with a description of various electrochemical techniques with diagrams of cells, accounts of methodology to elucidate electrode reaction mechanisms, discussion of reversibility of various kinds, even an introduction to spectroelectrochemistry. This is much more practical in content. Then follows treatment of more specific measurements, with discussion of electrochemistry in systems with coupled protons, an account of the electrochemistry of mixed valence systems, a description of electrochemistry at high pressures and finally an interesting review of ligand electrochemical parameters. Consequently this part of the book deals with both practical aspects of the subject and short reviews of areas that have developed in the last few years. It is not a guide to electrochemistry theory or practice.

The discussion on X-ray diffraction is short and to the point. Essentially it summarises the advances in the technique that analytical methods have made in the last couple of decades. There is no discussion of results and only 17 references. The treatment of neutron diffraction is even more cursory, but it includes a selected list of coordination compounds that have been studied by this method. Quite what this kind of review achieves is disputable, though it does provide a list of basic references that would be of use to a beginner in the field.

The second section begins with a short overview of ligand field theory (LFT), but again this is really for the specialist, and it says quite clearly that LFT as a research tool has a limited future, though it will continue to be useful in teaching. Then follows a series of descriptions of computational methodologies, assessing their advantages and limitations. Included are the angular overlap model, molecular mechanics, (with extensive references), DFT, SCF MO theory and methods, valence bond interaction models, and a range of more specific themes, such as topology, solvation and calculation of electrode potentials. No one, least of all the reviewer, can be expert in all these areas, but it does appear that the target audience is the experienced researcher seeking to broaden his expertise, and certainly not the beginner. Such a person will find adequate references to guide further reading, but it seems to be generally assumed that the reader, certainly mathematically adept, is already familiar with many of the concepts. However, this section is useful for emphasising the advantages and limitations of the various methodologies.

Section 3 is very short. It summarises the uses of various kinds of program and computation that have been applied to transition-metal complexes and it finishes with a selected list of available software packages and their sources. This section is likely to date quite rapidly, but no claim is made to comprehensiveness.

The final Section 4 consists of 8 reviews selected so as to illustrate the methodologies outlined in the preceding nearly 700 pages. These are competent and informative, but they may well be lost in a volume that is not clearly signalled as a review volume dealing with descriptive chemistry. They might have done more good being published elsewhere in *CCCII*. The first deals with spectroscopy and electronic structure of complexes $[FeX_4]^{n-}$. These are of biological import, and (apart from the use of discarded terminology such as ferrous and ferric) illustrate well what is currently understood of their properties. Then follow reviews of mixed-valence dinuclear species taking the Taube complexes as an example, mixed-valence clusters, that deals with the electrochemistry and spectroelectrochemistry of similar species, photochemistry multi-emission studies of rhenium(I) complexes, molybdenum nitrosyl and oxo complexes, that is concerned with the interaction of different metal centres, hexametal polynuclear metal clusters containing oxide ions, centred cage zirconium compounds, and some perspectives regarding dicyanamidebenzene and related materials. These reviews are all written by specialists, and will be of considerable value to selected individuals. Whether they are best placed in this volume is open to doubt.

In summary, this volume will be of use to advanced researchers wishing to extend their areas of expertise. It will not be useful to undergraduates or many graduate students. The editors are to be congratulated on including this volume in *CCCII*, though it may not achieve the use of other volumes, which may be employed to find specific information on particular compounds. It does, however, give an insight into the physical and theoretical techniques used in coordination chemistry at the beginning of the twenty-first century.

G.J. Leigh

Volume 3. Coordination chemistry of the s, p, and f elements, volume editor G.F.R. Parkin

Taken together, these chapters bring up-to-date and extend the reviews published in *CCCI*; the coverage supplements, rather than replaces, that of the earlier work. In most of the chapters the subject is set out in a systematic way according to donor atom, from Group 14 to 17, with simple donor ligands first, then chelating and, sometimes, macrocyclic ligands. It is easy for a reader to find information about a particular ligand and a particular metal.

Chapter 1 (79 pages, 799 references), on the Groups 1 and 2 metals, is impressive and authoritative. The author, T.N. Hanusa, cites four trends since the mid-1980s: the increased use of bulky ligands, the recognition of the importance of non-ionic interactions, the reappraisal of the "spectator" status of s-block ions, and the application of computational (especially DFT) methods. Stimuli have been provided by advances in bioinorganic chemistry, the use of new materials, e.g. superconductors, and the development of cryptands for the processing of nuclear fuel. Macrocyclic compounds are covered only briefly, since these topics are dealt with in *CCC1* and *Comprehensive Supramolecular Chemistry*.

Chapter 2 (78 pages, 1135 references), by S. Cotton, covers scandium, and then yttrium and the lanthanides taken together, in long dense paragraphs with few structural formulae. The chapter is crammed with useful information but there are few general insights and indications of how the subject area is changing over time. Much research has been prompted by the use of coordination compounds in magnetic resonance imaging and spectroscopic probes.

Chapter 3 on the actinides (139 pages, 1046 references) is a detailed and scholarly account written by teams from Los Alamos National Laboratory and the University of Alabama. The longest section (120 pages) covers the early actinides, thorium to plutonium. Each of the oxidation states III–VII is dealt with in turn and much information is compressed into tables. Not surprisingly, the literature is dominated by work on coordination compounds that are important in the extraction and separation of actinides on an industrial scale, and in land remediation. The emphasis is on compounds containing oxygen donors, e.g., carbonates, nitrates, sulfates and phosphates, as well as a huge range containing chelating ligands. Much less is known about the later actinides, americium to nobelium, but it is pointed out that these highly radioactive elements are known mainly through their coordination compounds, which are often the first derivatives to be studied.

Chapter 4 (33 pages, 118 references) by G.H. Robinson is an interesting and authoritative, but rather discursive and more loosely written, account of current developments in the organometallic chemistry of aluminium and gallium. The story is fascinating as new bonding types are displayed and new challenges to conventional wisdom presented, but it cannot be described as a systematic survey of coordination compounds. There is nothing about aluminium or gallium complexes in water or other oxygen-containing solvents, halide complexes in molten ionic solvents, or biocompatible complexes, all of which are important in industry or environmental chemistry and might be expected to find a place in a book about "comprehensive" coordination chemistry.

In the chapter on indium (42 pages, 460 references) and thallium (25 pages, 350 references) H.V. Rasika Dias returns to the pattern of the earlier chapters. The coverage and presentation are excellent and subheadings are skillfully used to make it easy for readers to find their way around. Topics of special interest include precursors for CVD syntheses of nitrides and sulfides, porphyrin complexes, tris(pyrazolyl)boronato derivatives, complexes containing carbene ligands, ^{111}In radiopharmaceutical reagents, and complexes containing metal–metal bonds, in which the formal oxidation state of the metal is I or II.

In the chapter on arsenic, antimony and bismuth by W. Levason and G. Reid (69 pages, 623 references) the two common oxidation states III and V are considered together, but since very few coordination compounds of As^{V} and Bi^{V} have been isolated it is only in the section on antimony that there is much to say about the higher oxidation state. Good use has been made of tables. Many of the figures have been reproduced from published sources and this has led to a poorer standard of presentation than is found in the other chapters, where most of the figures have been redrawn.

In Chapter 7 (54 pages, 544 references) by J. Parr the emphasis is on compounds of germanium, tin and lead having donor atoms from Groups 15 or 16. There is a short section on halide complexes and organometallic compounds are included only when the introduction of organic groups as ligands stabilises species with interesting coordination environments. For each donor configuration, compounds of the three elements and the two common oxidation states are considered together but only for tin are the stabilities of the two oxidation states sufficiently evenly matched for the isolation of Sn^{II}–Sn^{IV} species.

CCCII will now become the first place to look for information on coordination compounds involving donor atoms from Groups 15–17. *CCCI* will remain the primary source for compounds of aluminium and gallium, which have been treated differently from the other elements.

J.D. Smith

Volume 4. Transition metal groups 3–6, volume editor A.G. Wedd

As the volume editor observes in his introduction, there has been a huge surge of activity in early transition metal coordination chemistry since the publication of *CCCI* in 1987. Thus it is good to see that recent, exciting developments in areas such as metallafullerene chemistry, alternative (non-carboyclic ring based) precatalysts for olefin polymerisation, mesoporous materials, and vanadium and Group 6 bioinorganic chemistry are all well-represented and well-referenced in the chapters on the relevant elements. In the text, Sc and Y, Zr and Hf, and Nb and Ta are discussed together, whilst the remaining elements merit individual chapters; as in the previous edition, compounds are classified according to oxidation state, with further subdivisions based on ligand type. The final four chapters deal with dinuclear metal–metal bonded systems, polyoxo anions, polyoxometallates and chalcogenide-containing metal clusters, again areas that have expanded dramatically since *CCCI*. In general, pure organometallic compounds are not discussed in this volume, although the distinction between organometallic and coordination chemistry can obviously be blurred and important organometallic fragments (e.g., alkylidenes and alkylidynes) on metal centres supported by 'classical' ligands are naturally included.

This volume is not without it faults. The decision to exclude the lanthanide elements from the Sc and Y chapter is strange since traditionally (and rightly in my view) these chemically very similar elements have always been discussed together. This chapter, although well referenced (258 references), is correspondingly rather short, some 25 pages out of 815. Moreover, lanthanide coordination chemistry is to be found in Volume 3 of the series (Coordination Chemistry of the s, p, and f Metals) in a chapter entitled "Scandium, Yttrium, and the Lanthanides"! At best this is likely to be confusing, and may also have resulted in unfortunate duplication of material. The quality of reproduction of many of the X-ray structures is rather poor, and lacking in atom labels in some cases, and there are several typographical (e.g., chrom- uim in a section title!) and diagrammatical errors. Also, whilst it is inevitable perhaps that some literature omissions will occur in a volume of this size, this reviewer was surprised to note the lack of any reference to the work on cleavage of dinitrogen by diamidoamine vanadium complexes (*J. Am. Chem. Soc.*, 1999, **121**, 10444) in the chapter on vanadium. Nonetheless, although the cost will probably prohibit private ownership, this volume will be a valuable addition to libraries and a very useful resource for research groups in the area.

F.G.N. Cloke

Volume 5. Transition metal groups 7 and 8, volume editors E.C. Constable and J.R. Dilworth

For Group 7 elements, a single chapter is devoted to each and, notably, technetium is included for the first time. Each of the three chapters is then subdivided into sections primarily based on the formal oxidation states of the particular element. However, for the Group 8 elements, there is one chapter concerning iron, whereas ruthenium and osmium are treated together in two chapters. The first describes low-oxidation-state complexes of Ru and Os, while the second details high-oxidation-state complexes. This disorder in approach to describing the coordination chemistry associated with the two groups is symptomatic of the difficulty in collecting such a large amount of data and compiling contributions by a wide variety of authors. The first chapter of this volume, ca. 110 pages, is devoted to manganese and, as the editors confess, is less comprehensive than desired and is certainly the weakest of all the six chapters. There are, however, excellent sections to be found on oxo-clusters containing mixed Mn^{IV}/Mn^{III} systems, dinuclear clusters based on Mn^{III} and macrocyclic ligands containing Mn^{IV}, Mn^{V} and Mn^{VI} centres. The chapter ends with a well-written description of the bioinorganic role of manganese and cites over eight hundred articles and books.

Unlike the other chapters in this volume, which attempt to cover the literature since the publication of *CCCI*, the second chapter, ca. 130 pages, describes the coordination chemistry of technetium and begins with a description of the discovery of the element in 1937. This element was not included in the previous edition. A short introduction to the generation and radiopharmaceutical applications of ^{99}Tc follows. The chapter is also divided into sections based on formal oxidation states with the sections devoted to Tc^{VII} and Tc^{VI} containing complexes predominately describing oxo-, nitrido- and a few imido-derivatives. As might be expected, the section concerned with Tc^{V} is the largest. In addition to the three sections describing the oxo-, nitrido- and imido-derivatives, hydrazido, diazenido and diazene are dealt with. There is a brief section devoted to the relatively rare coordination chemistry of Tc^{IV}. The three remaining subsections are devoted to the lower oxidation states Tc^{III}, Tc^{II} and Tc^{I}. These include softer ligands such as phosphines, arsines, thionitriles, carbonyls, isocynides and derivatives containing multiply-bonded Tc centres. Curiously, this first main section ends with a very useful review of ^{99}Tc NMR spectroscopy. The final section describes the radiopharmaceutical applications of coordination complexes of Tc and is subdivided into sections concerning the Tc complexes employed to image the major organs of the human body and also a section on multi-drug resistance. This chapter

ends with the citation of over seven hundred articles and books.

The third chapter, ca. 100 pages, is a review of the coordination chemistry of Re since 1987. This chapter is arranged as previously described for Tc, i.e., according to formal oxidation state. Initially the subsections are divided into ligand type with the oxo derivatives predominating in the higher states but with sulfido-, nitrido- and imido-derivatives also included. From Re^{IV} onwards the ligand types are divided into those "Complexes containing exclusively monodentate ligands" and "Complexes with chelating ligands" – at least until the section describing the relatively rare Re^{II} derivatives, which is subdivided into two, entitled "P-donor ligands" and "N-, and S-donor ligands". For Re^{I}, chelating ligands containing N or P constitute the main examples, although isocyanides and tricarbonyl derivatives also feature prominently in this section. For Re^{0}, thionitrosyl, hydrazido and hydrido ligands are also included, in addition to the more conventional N-, P-, and As-centred ligands. This chapter concludes with a brief section entitled "Re Compounds and Nuclear Medicine" and the citation of over 1200 articles and books.

The following chapter, ca. 120 pages and dedicated to the coordination chemistry of Fe, abandons the format of organising the sections by oxidation state and instead begins with a series of brief sections purporting to deal with a variety of topics including, bioinorganic redox systems, magnetic materials, pigments, intramolecular electron-transfer, spin cross-over complexes, spectroscopy, kinetics and mechanisms, size and solvation, stability constants and speciation, nutrition metabolism and pharmacology, and geochemical and environmental aspects. The main body of this review follows in sections entitled "Group 14 Donors", "Group 15 Donors", "Group 15/16 Donors", and "Group 16 Donors", all of which cover the preparation, characterisation and subsequent reactivity studies of Fe derivatives containing macrocyclic ligands, based chiefly on N- and O-donor atoms. While the Group 14 section mentions cyanoferrates and carbonyl derivatives very briefly, the carbonyl cluster chemistry of Fe is omitted. The sections dedicated to Group 15- and 16-based ligands dominate this chapter. Once again little emphasis is placed on ligands such as amines, thiocyanates, azides, N_2, NO, O_2, phosphines, alkoxides, peroxides and superoxides. Given that an estimated two-thirds of the ca. 1500 cited references deal with this topic, the entire chapter would be better entitled "The Macrocyclic Chemistry of Fe".

The penultimate chapter, ca. 150 pages, focuses on both Ru and Os in the formal oxidation states of II and III. The higher oxidation state is covered initially by a seventeen-page review. There follows an excellent and comprehensive account of the photochemical and photophysical properties of complexes of the type $[Ru(bipy)_3]^{2+}$, $[Ru(bipy)_2L_2]^{n+}$, and $[Ru(bipy)L_4]^{n+}$ (bipy = 2,2′-bipyridine or analogues). In addition, this review is extended to include bimetallic- and trimetallic-containing systems and other N-based ligands including phenanthroline, trispyrazoylboranes, and porphyrins. There is also a brief reference to models for photosystem II. The review concludes by examining both P- and S-based ligands, predominantly chiral diphosphines, and multidentate thiols. There is a relatively sparse section concerning dihydrogen complexes, and once again the carbonyl cluster chemistry is omitted from the scant half-page section devoted to the chemistry associated with the oxidation state 0 derivatives. The review ends with the citation of almost two thousand articles and books. On a minor point, the reviewer welcomed the (almost) consistent use of the word "spectroscopic" to qualify *data* or *timescales* when referencing both NMR and ESR spectroscopic experiments. This was irritatingly absent in previous chapters.

The final chapter, ca. 100 pages, is devoted to higher oxidation state [IV–VIII] coordination compounds of Ru and Os. The structure of this chapter reverts to the more traditional format of *CCCI* where the sections are divided by oxidation state. The first two sections which deal with oxidation states VII and VIII and the fourth, which deals with oxidation state V are, as expected, relatively short. Their subsections are mainly concerned with imido-, nitrido-, and oxo-ligands. The third section which describes the tervalent state is approximately six times longer than the others and is dominated by a extensive subsection dealing with the electrochemistry associated with complexes of the type $[M(O)_2(bipy)_2]^{2+}$. Pourbaix diagrams, tables of formal potentials, and cyclic voltammograms are all included. This report is extended to include other ligand systems in addition to bipyridyls, including macrocyclic amines and monodentate ligands such as phosphines. The complexes discussed in this section are mainly nitrogen-based ligand systems, e.g., amido, nitrido, imido, cyanoimido, azdoimido, hydrazido, and porphyrins. A small number of other Group 15-based ligands are also presented. A subsection is devoted to the electrochemistry of complexes of the type $[M(O)(bipy)_2(L)]^{2+}$. Both monomeric- and dimeric species are discussed. The chapter ends with brief descriptions of M^{IV} complexes containing oxygen or sulphur as ligating atoms, or halides and hydrides. Some 600 articles and books are cited.

To comment in general, I do not envy the editors who undertook the task of assembling this particular volume, given the expansion in breadth and depth of chemistry associated with the coordination complexes of these two groups since the publication of the first edition. Unfortunately, the apparent strategy of allocating approximately the same page limit to each chapter does not reflect the relevant importance of their chemical and biological significance. Thus some chapters fail to cover the breadth associated with the coordination chemistry of a key element, while for certain other elements the

treatment is overly detailed. The rationale for the segregation of the subsections is also not always apparent and, for a given author, it may vary between sections devoted to different oxidation states. It is also confusing that, when identical topics have been chosen, the titles differ. For example, in the chapter devoted to Tc a subsection is entitled "Compounds containing no multiply bonded ligands" while the corresponding subsection in the Re chapter is entitled "Complexes containing exclusively monodentate ligands" – a little more consistency should have been imposed by the editors. Such consistency would have removed the repeated debates in each chapter by the relevant author(s) as to what exactly was meant by the term "organometallic compound" and whether to include multiply-bonded species or not.

To my relief, the poorly reproduced scanned ORTEP diagrams were few and limited to the first chapter. The interested reader or aspiring author of any similar future volume is directed to the contrast in clarity of Figures 13 and 14. In summary, this volume contains some excellent sections that will be invaluable to researchers in the area, but comprehensive it is not!

G.A. Lawless

Volume 6. Transition metal groups 9–12, volume editor D.E. Fenton

This volume deals with the chemistry of the platinum group metals, copper silver and gold, zinc, cadmium and mercury. It is somewhat marred by lack of a chapter on rhodium, which, since it is a personal favourite in my own work, I did find disappointing. The literature coverage starts from about 1982, and there is an assumption that a reader will have access to *CCCI*. The organisation of the chapters largely follows oxidation state and then ligating atom, with further subdivision depending on the number of coordination sites of the ligands.

The chapters deal with cobalt (P.V. Bemhardt and G.A. Lawrance; 146 pages, 1439 references) iridium (L.J. Yellowlees and K.G. Macnamara, 100 pages, 758 references) nickel (F. Meyer and H. Kozlowski, 308 pages, 2579 references), palladium (N.M. Kostić and L.-M. Dutcă, 118 pages, 994 references), platinum (L.M. Rendina and T.W. Hambley, 74 pages, 586 references) copper (R. Mukherjee, 164 pages, 588 references), silver and gold (M.C. Gimeno and A. Laguna, 236 pages, 3330 references), zinc (S.J. Archibald, 106 pages, 1002 references) references). This is followed by a 28-page index, perhaps inevitably for a volume of this size, not entirely satisfactory. For example, neither orthometallation nor cyclometallation is listed, despite the large number of palladium complexes of this type that are discussed. There is no general glossary of acronyms, but curiously a local one in the iridium chapter. In the palladium chapter, but not in others, there is a useful list of the major reviews published during the period of coverage.

All the chapters are characterised by their systematic organisation, attention to detail, and real thoroughness of coverage. The literature references run through 2002, and in some chapters into 2003 – this is an exceptional bibliography. The diagrams are largely clear and readable, and the editors are to be congratulated on allowing the authors enough space to present complex structures in a genuinely comprehensible way (particular commendations for the copper chapter); journal editors, pressed for space, frequently shrink these to an extent that the even slightly myopic are reaching for magnifying glasses. A few crystal structures are a little fuzzy in appearance (for example, on page 568), perhaps due to conversion from colour to black and white, but this seems to be confined to the palladium chapter. Any inorganic chemist will find much of interest here, and this series will, without doubt, become a standard reference work. When will *CCCIII* be coming along – will the intervals get shorter as the information flow becomes ever more unmanageable? The choice of material covered in any chapter will not suit everyone – I would have liked to see more of the literature on platinum anti-tumour compounds, for example, but no volume will please everyone on every topic. The volume will be used mainly by research workers aiming to catch up on literature, or to start to work with new classes of compound; it is beyond undergraduates and indeed probably many graduate students. Overall a massive and impressive piece of work, but, alas, with a large rhodium shaped hole in it.

P.A. Chaloner

Volume 7. From the molecular to the nanoscale, volume editor C.A. Creutz

This volume provides a substantial *tour de force* of the increasingly important contributions of coordination chemistry to the rapidly emerging fields of nanoscience and technology. The 'bottom-up' approach of synthesising multifunctional and multistable nanostructures with tailored properties is naturally suited to well-established coordination chemistry approaches as the variety of metal–ligand interactions can be utilised to provide molecular-based assemblies of increasing complexity, both in structure and in function, from the molecular to the nanoscale.

The range of subjects covered in this volume is large and varied. Advances in both synthetic techniques and in characterisation of structural and physical properties are exhaustively catalogued and/or expertly reviewed. Several of chapters first deal with high nuclearity clusters, encompassing polyoxoanions, metal–chalcogenide polynuclear systems and cyano- and oxalato-bridged

assemblies among others. The overview of coordination systems then continues with chapters surveying coordination polymers and the design of supramolecular networks by utilising the powerful self-assembly and templating approaches. The emphasis then shifts to liquid crystal systems with an impressive overview of multifunctionality, where the metal-based properties are combined with those of mesogenic systems, and the synthetic part of the volume concludes with the utilisation of sol–gel processes to fabricate materials such as glasses and thin films. The last three chapters deal with electron-transfer and magnetism in metal complex-based molecular assemblies, arguably two of the most important prevailing themes in the historical development of coordination chemistry. The importance of the study of electron-transfer processes will continue to be dominant in the coordination chemistry field in the foreseeable future, as for instance both energy-conversion and biotransformation issues are tackled, while single molecule magnets may represent target systems for satisfying our society's quest for ever increasing capacity for magnetic information storage.

Overall I found this volume a pleasure to read and I recommend it as a most valuable addition to the library resources of any active research chemist in the fields of inorganic and materials chemistry.

K. Prassides

Volume 8. Bio-coordination chemistry, volume editors L. Que and W.B. Tolman

The editors are internationally recognised experts within this area. They begin the volume with a first chapter that acts as an introduction to the volume as a whole, stressing the ever-increasing database of metalloenzyme active sites and providing a very useful gallery of active-site motifs that are common to groups of metalloprotein systems that may have diverse functions. A further 28 chapters, separately written by experts in the subjects that they address, then follow. These chapters have been grouped in loosely related areas, as discussed below.

Chapters 2–4 are concerned with the nature of the metal sites that are involved in electron-transfer. Chapter 2 describes biological aspects of cytochromes, Chapter 4 biological aspects of cupredoxins and model inorganic complexes that relate to them, whilst Chapter 3 concentrates on the inorganic chemistry of iron–sulfur clusters. Chapters 5–9 encompass systems that are mainly concerned with the transport and storage of metal ions in biology. These include alkali and alkaline earth ion transport and storage (Chapter 5), siderophores and transferrins (Chapter 6), ferritins (Chapter 7), metal ion homeostasis (Chapter 8) and metallothioneins (Chapter 9). In this thematic group, most attention is again paid to the biological systems, particularly to X-ray structures where known, but reference is made to synthetic model complexes where appropriate. This approach is followed throughout the rest of the book.

There is a wide range of metalloproteins that are concerned with binding, transporting and activating dioxygen and with carrying out oxidation chemistry with or without direct involvement of dioxygen. Chapters 10–18 are concerned with these systems. Included here are dioxygen-binding proteins (Chapter 10), heme-peroxidases (Chapter 11), cytochrome P450 (Chapter 12), non-heme di-iron enzymes (Chapter 13), non-heme mono-iron enzymes (Chapter 14), dicopper enzymes (Chapter 15), monocopper oxygenases (Chapter 16), multimetal oxygenases (Chapter 17) and molybdenum and tungsten enzymes (Chapter 18). Also concerned in the area of dioxygen biology are superoxide processing systems (Chapter 19) and photosynthetic evolution of dioxygen (Chapter 20).

The biochemical activation of the small molecules dihydrogen (hydrogenases) and dinitrogen (nitrogen fixation) are discussed in Chapters 21 and 22 respectively, whilst Chapter 23 is concerned with zinc hydrolases and Chapter 24 with dinuclear hydrolases. The remaining chapters are concerned with the bioorganic chemistry of cobalt and nickel (Chapter 25), metal-radical arrays (Chapter 26), iron–sulfur clusters in enzyme catalysis (Chapter 27), denitrification (Chapter 28) and finally DNA and RNA as ligands to metals (Chapter 29). There is a comprehensive volume subject index.

The content of the chapters generally dates up to 2002 and each chapter is well referenced. In general the chapters are sensibly grouped, given the wide and diverse range of systems that are encompassed, although the two chapters on Fe–S systems would have been better placed together, rather than well separated.

The book as a whole is very well produced and lavishly illustrated. For some years to come it will provide a very useful source of reference material for research workers and teachers in this highly active and diverse area of chemistry.

R.L. Richards

Volume 9. Applications of coordination compounds, volume editor M.D. Ward

The volume editor is to be congratulated, both on his selection of topics and his choice of contributing authors. The latter, among leaders in their fields, in turn deserve great credit for producing this impressive volume. In his preface, Ward points out that the emphasis is on breadth rather than depth, with extensive citations

to more detailed reviews, monographs and books. This caveat is inevitable because of the vast quantity of material available on the applications of coordination compounds, particularly so, perhaps, in the area of catalysis which covers 50% of this book.

There are 23 chapters. Eleven are devoted to metal complexes in organic catalysis. The first seven deal with organic reactions of unsaturated organic compounds in: polymerisation (V.C. Gibson and E.L. Marshall; 74 pages, 1004 references), hydrogenation (C. Pettinari, F. Marchetti and D. Martini; 64 pages, 429 references), addition of CO (P.W.N.M. Van Leeuwen and C. Claver; 65 pages, 690 references); oxygen, nitrogen, and carbon-atom transfer (T. Katsuki; 57 pages, 300 references); HX (X=B, CN, Si, N, P) addition to CC multiple bonds (M.K. Whittlesey; 39 pages, 203 references), C–C cross-coupling (I.P. Beletskaya and A.V. Cheprakov; 68 pages, 522 references), and C-heteroatom cross-coupling (J.F. Hartwig; 29 pages, 226 references). S. Kobayashi, Y. Mori and Y. Yamashita deal with metal complexes as Lewis-acid catalysts in organic synthesis (45 pages, 371 references). The next three relate to catalytic procedures involving: supported metal complexes (F. Quignard and A. Choplin; 25 pages, 193 references), electrochemical reactions (A. Deronzier and J.-C. Moutet; 36 pages, 528 references), and combinatorial methods (M.T. Reetz; 39 pages, 124 references). The five following deal with optical properties of coordination complexes as: speciality dyes and pigments (P. Gregory; 30 pages, 82 references), dyes for optical storage and electrochromic materials (R.J. Mortimer and N.M. Rowley; 38 pages, 228 references), nonlinear optical materials (B.J. Coe; 66 pages, 641 references), phosphors (J. Silver; 28 pages, 283 references), and dye-sensitised nanocrystalline TiO_2 cells for conversion and storage of solar energy (Md. K. Nazeeruddin and M. Graetzel; 39 pages, 112 references). This is followed by a discussion of metal complexes for hydrometallurgy and extraction (P.A. Tasker, P.G. Plieger and L.C. West; 49 pages, 395 references). The four penultimate chapters are concerned with medical and biomedical applications, covering metal complexes as: drugs and therapeutic reagents (N. Farrell; 31 pages, 280 references), MRI contrast and enhancement agents (É. Tóth, L. Helm and A.E. Merbach; 40 pages, 210 references), radioactive metals in imaging and therapy (S.Z. Lever, J.D. Lydon, C.S. Cutler and S.S. Jurisson; 28 pages, 239 references), fluorescent complexes for biomedical applications (S. Faulkner and J.L. Matthews; 31 pages, 176 references), and photodynamic therapy (R. Bonnett; 57 pages, 412 references). Complexes as precursors for semiconductor films and nanoparticles are discussed by P. O'Brien and N.L. Pickett (58 pages, 418 references) as the topic of the closing chapter, which is followed by a subject index (43 pages). The majority of the chapters have references to papers published in 2002; particularly prolific in this respect are Chapters 1, 6, 14, 17 and 28.

Comparison with *CCCI* shows; (i) an entirely new group of authors, (ii) little overlap in topics and (iii) much greater emphasis on catalysis. As for (ii), where chapter headings in *CCCI* and *CCCII* are similar, there is negligible overlap. For example, Chapter 17 (hydrometallurgy and extraction) is particularly rich in recent bibliographic data, reflecting the increased current importance of ecological issues; Chapter 8 (Lewis-acid catalysts) has a far greater applicational and organic chemical flavour than its forerunner in *CCCI*; Chapter 12 (dyes and pigments) has only about a quarter of its references prior to 1987. The principal difference between the two editions is in the relative emphasis on catalysis: (in *CCCII*, 546 out of 1063 pages; in *CCCI*, 386 out of 1030 pages); inevitably these topics are covered elsewhere in the organometallic and organic chemical literature, some in much greater detail. Nevertheless, the material of Chapters 1–11 is of very high quality; this reviewer was particularly impressed with Chapter 1 among chapters dealing with reaction types and Chapter 11 of those dealing with catalytic methodology.

In summary, this is an extremely valuable addition to the chemical literature. It demonstrates the vast scope and remarkable range of current applications of coordination compounds over diverse fields, ranging from the biological/medical to that of materials.

M.F. Lappert

Volume 10. Cumulative subject index

This subject index covers 266 pages. It appears to be a compilation of the individual subject indexes that appear in each separate volume. Although there is no compound index, here or in the individual volumes, the index is detailed enough to allow a rapid search of the contents of *CCCII*. Of course, an author index, apart from one detailing the contributors to this work, would be impossibly large and the publishers have wisely decided to eschew one, either here or in the separate volumes. Somewhat bizarrely, the two-page preface that is reproduced in every volume is included at the beginning of this volume too, though why anyone should look for it here is not obvious. This is followed by a further two pages of "thoughts" on the state of coordination chemistry gleaned from the International Advisory Board. These are not breathtakingly unexpected, and one wonders why they were included in every volume as well as before the index.

G.J. Leigh

Summary

In the 1920s Mellor started to publish his sixteen-volume compendium on inorganic chemistry. This was meant to be completely inclusive and that was probably the last occasion upon which such a Victorian project was really feasible. Despite the title of this compendium, *CCCII*, the editors have wisely refrained form trying to present a comprehensive account of coordination chemistry and have generally restricted the attention of the various authors to the time since *CCCI* was concluded. In addition they have excluded most (but not all) of transition metal organometallic chemistry, and though one understands why, this seems rather arbitrary. Indeed, whether a comprehensive account of such an enormous topic as coordination chemistry is really feasible, and whether it is desirable in view of the availability of electronic databases is questionable. The publishers of Gmelin have long since given up the fight to provide comprehensive accounts. Nevertheless, the general editors might have provided more precise guidelines on what to exclude and how to present the material. Of course, what a database cannot provide is a critical account of a given field, such as an experienced practitioner can vouchsafe, and it is this aspect of *CCCII* that should be of more continuing value. The editors and authors are generally established authorities in the various facets of modern coordination chemistry.

The volumes can be divided roughly into two groups, those that provide accounts of the chemistry of particular elements (volumes 3, 4, 5,and 6), and the rest, which discuss techniques and methods, and specific areas. The factual material presented clearly contains several lacunae, as the individual reviews above make clear. However, the response appears to be generally positive, and these volumes should be of use to new and established researchers for some years to come. The volumes in the second group are of more variable value. Clearly discussions of ligands and preparations are likely to be useful to many researchers, though whether one would automatically choose *CCCII* as a source book is questionable. Volumes describing techniques and developments in techniques are likely to become outdated quite rapidly. Volumes 7, 8 and 9 have been particularly well received by the reviewers, and this may well be because they provide wide-ranging accounts of areas to which coordination chemistry is relatively new. One is tempted to wonder whether a future *CCCIII* might not be better presented as a series of review volumes of this type, eschewing the more descriptive volumes. Whatever the content, the enormous lists of literature citations in *CCCII* are likely to be of value for some years to come. The reviewers concur that the volumes have been produced to a high standard, and that every chemistry library should have a copy available.

G.J. Leigh
Department of Chemistry, School of Life Sciences
University of Sussex, Falmer, Brighton BN1 9QJ, UK
Tel.: +44-1273-606755; fax: +44-1273-67849