

Expanded Coordination Chemistry

COMPREHENSIVE COORDINATION CHEMISTRY II. FROM BIOLOGY TO NANOTECHNOLOGY

Volume 6 TRANSITION METAL GROUPS 9–12

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The original “Comprehensive Coordination Chemistry” was published in 1987 and since then the field has expanded massively. This new edition covers developments since 1982. There is now so much literature that a comprehensive review is not possible, so particular areas of interest have been selected. As with the first edition, in these volumes organometallic compounds have been excluded. These are defined as compounds where metal-carbon bonds are greater than half the coordination number of the metal. Such organometallic compounds are covered in a companion work, “Comprehensive Organometallic Chemistry”.

Altogether there are 10 volumes in the set, with the last one comprising indexes. Volumes dealing with the platinum group metals will be reviewed.

Volume 6 aims to be nearly comprehensive in its coverage. The coordination chemistry of the elements: Co, Ir, Ni, Pd, Pt, Cu, Ag, Au, Cd and Hg is covered. Rhodium, unfortunately, is not covered due to factors beyond the Editors’ control. In most chapters, the chemistry is ordered by the metal oxidation state and then by the ligand donor atom. Applications are only briefly described as they are covered in more detail in Volume 9.

P. V. Bernhardt and G. A. Lawrance review cobalt chemistry, referring to secondary references as there are 18,000 primary references for the period covered. The biological chemistry of cobalt and its applications are discussed, including cobalamins and non-corrin proteins. A table of ligand lability rates is included. Industrial applications for organic transformations such as oxidation, carbonylation, hydroformylation and cycloadditions, and cobalt in electrocatalysis and analytical sensors are reviewed.

Iridium chemistry is discussed by L. J. Yellowlees and K. G. Macnamara. The majority of the coordination chemistry concerns iridium(III). There is an emphasis on structural data. Biological complexes of iridium(III) and iridium(I) are dis-

cussed and there is a short section on the catalytic activity of iridium(III) complexes and a detailed table of iridium(I) catalytic systems.

F. Meyer and H. Kozłowski contribute a non-comprehensive review of nickel coordination chemistry, with sections on bioinorganic and materials chemistry. There are many nickel-dependent enzymes and complexes with macrocycle and porphyrin ligands. Structural features of nickel(II) complexes are discussed and data on the electronic absorption spectra and electrochemical data of nickel(II) macrocycles is tabulated. Complexes with bioligands: models for the carcinogenic properties of nickel, are covered. Structural data on nickel(0) phosphine complexes are provided.

The chemistry of palladium is reviewed by N. M. Kostić and L.-M. Dutcă. In some places, the text of this chapter is rather difficult to understand. There is a useful survey of review articles on palladium. Applications of palladium chemistry that are mentioned include the use of palladium acetylacetonates for thin film deposition, the use of palladium phosphine complexes in catalysis and the use of palladium(II) complexes for peptide hydrolysis. Dendrimers, polynuclear systems and palladium nanoparticles are all discussed.

L. M. Rendina and T. W. Hambley review the chemistry of platinum. As in other chapters, the authors have not attempted a comprehensive survey because of the size of the field. However they provide a flavour of the current state of platinum chemistry. There is a section on oxidative addition reactions to platinum(0) which are models for catalytic reactions such as hydrosilation. Reactions of ligands coordinated to platinum(IV) are discussed, as are the kinetics and mechanism of platinum(IV) reduction.

R. Mukherjee reviews major developments in copper chemistry, focusing on structural aspects and magnetic behaviour. Structural data is tabulat-

ed by ligand type. There is emphasis on the modelling of biological systems.

M. C. Gimeno and A. Laguna review silver and gold chemistry – separately although combined in one chapter. There is a discussion of the chemical differences between silver and gold. The chemistry of gold mainly concerns oxidation states (III) and (I). A number of gold complexes have interesting luminescence properties and some show biological activity. Gold(I) thiolates in particular have anti-tumour, antiarthritic and antimicrobial activity. They are also used to make gold films.

An overview of key results in zinc chemistry, by S. J. Archibald, has an emphasis on X-ray structural data. As zinc(II) is the only significant oxidation state, the review is subdivided by ligand type. Many complexes serve as models of biologically active zinc systems, for example, complexes with mixed donor ligands are models for liver alcohol dehydrogenases. Zinc macrocycle complexes are in a separate section. Applications in pharmaceuticals, catalysis and the fluorescent detection of zinc in cellular systems are discussed and there is a section on the biological chemistry of zinc.

D. K. Bretinger reviews cadmium and mercury, including methods used to study their coordination chemistry. Their complexes, in particular inclusion

complexes such as $\text{Cd}(\text{CN})_2$, are reviewed. As the chapter contains a lot of structural description, I felt more diagrams would have been helpful.

Reading Volume 6 gives an overview of the vast area of coordination chemistry and could be a useful source of ideas for the synthetic inorganic chemist. The enormous amount of literature generated in the past 25 years means that the authors had a very challenging task. In a work of this size, a few typographical errors are inevitable and they do occur. The colour diagrams are helpful although they are segregated on pages in the middle of the book. Some of the diagrams, such as X-ray structures, are a little fuzzy. The number of potentially explosive perchlorate counterions still being used in synthesis is a cause for concern.

With modern search techniques, it is often easier to search for a substructure rather than consult a book of this size. However, computer searches can never capture the richness and diversity of coordination chemistry in the way that this volume does.

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Palladium Oxide Sensitiser for LPG Detector

Liquid petroleum gas (LPG): butane, propane or their mixture, is used as a fuel particularly in regions and activities where the usual utilities are missing. It is used commercially and domestically for space and water heating, cooking, lighting, and as an automotive fuel. It is sold and stored in refillable cylinders as a pressurised liquid. It is a clean versatile fuel (producing lower green house emissions than alternatives), but its flammability requires awareness and vigilant leak detection.

Zinc oxide (ZnO) or tin dioxide are common gas sensing materials usually with a thin layer of a noble metal (palladium (Pd) or platinum) to increase their catalytic activities and response times (1). Various methods are used to apply the catalyst layer to the substrate: salt decomposition, spraying, impregnation by salt solution, and CVD by sputtering or evaporation. Substrates have also been dipped into salt solution followed by evaporation. Optimisation of the noble metal catalyst layer and

its properties is critical to the success of a detector.

Now, scientists in India have found some optimum values for catalyst layers in a wet-chemical process where a Pd oxide sensitiser layer was formed on a thin ZnO film for LPG detection (2).

They found a sensitised film with stable resistance was formed after 15 to 20 dippings of a ZnO film into a PdCl_2 suspension. The room temperature resistance was a function of the amount of Pd loading. Stable sensors were fabricated with optimised Pd loading, with a suitable operating temperature $\sim 250^\circ\text{C}$. A sensitivity of 88% was observed for 1.6 vol.% LPG in air with a 15 s response and 60 s recovery. The fast response and quick recovery provides a useful domestic LPG alarm.

References

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