

It seems to me that every chemistry library should have this book, especially those serving laboratories which might consider using bismuth organic compounds for organic synthesis.

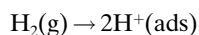
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Metal Oxygen Clusters. The Surface and Catalytic Properties of Heteropoly Oxometalates. By *John B. Moffat*. Kluwer Academic Publishers, Dordrecht 2001. 320 pp., hardcover € 170.00.—ISBN 0-306-46507-8

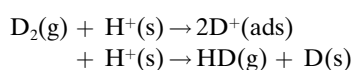
Heteropolyoxometalates are of considerable interest as catalysts for acid–base and redox reactions, and consequently this field continues to be studied intensively. Thus the book *Metal Oxygen Clusters* by John B. Moffat deals with a subject that is certainly topical at this time. The work is divided into eleven chapters. Chapter 1 gives a short account of the historical development of research on oxometalates. Chapter 2 discusses the synthesis of these compounds, but without giving detailed information. Chapter 3 is concerned with the physical characterization of oxometalates, describing the various methods used, with the help of examples. However, it is surprising that there is no mention of such important methods as Raman spectroscopy and inductively coupled plasma (ICP) spectroscopy. The structure of oxometalates and their bulk properties are described in Chapter 4, then Chapter 5 deals at considerably greater length with how their stability is affected by temperature and pH. Oxometalates are often used in the form of supported catalysts, and Chapter 6 describes the preparation, characterization, and properties of such systems for a wide variety of support materials. Chapter 7 is concerned with microporosity, sorption, and diffusion in metal–oxygen clusters, and with cation exchange processes. Special attention is given to the origin of microporosity and its dependence on the nature of the counterion. Oxometalates possess acidic

and redox properties, and accordingly Chapter 8 describes the study of their acidic properties by physical methods and reactivity tests. This chapter also contains a short section on redox properties. Two fairly long chapters are devoted to acid-catalyzed processes and oxidation reactions using oxometalates. The reactions discussed in Chapter 9 (acidic catalysis) are: conversion of methanol to hydrocarbons (MTG reaction), reactions of alcohols, conversion of alkanes into alkenes, alkylations and Friedel–Crafts reactions, ring enlargements, and ring contractions. Chapter 10 discusses oxidation reactions applied to alkanes, alkenes, methacrolein, and isobutyric acid. Chapter 11 concludes the book with a brief description of the use of oxometalates in environmentally relevant processes.

This book by J. B. Moffat gives a broad survey of the published work on oxometalates up to the beginning of year 2000. In a monograph dealing with a narrowly defined subject area the reader expects to find a critical evaluation of the published work, but unfortunately that is absent or only very limited here. Also none of the chapters ends with a summary or conclusions. Often there is a reference to other parts of the book, in a phrase such as “noted elsewhere”, without giving a page or section number. There are instances of unnecessary repetition in the text or figures—for example, Figures 5.4, 5.5, and 5.6 are identical to Figures 3.1, 3.2, and 3.3 respectively. SI units are not always used. Energies are usually given in kcal mol^{−1}, and only occasionally in the preferred unit kJ mol^{−1}. Many other lapses could be listed. For example, in Section 6.1.2 we read “...TiO₂ in the form of titania...”, and the catalytic activities observed for different catalysts are compared without specifying the quantities used and how they were normalized. In the stoichiometric equations on page 170:

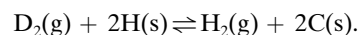


and on page 171:



the charge balance is incorrect. Also the book is unfortunately not free of printing

errors, of which I give here just one example:



The quality of the figures is not up to modern standards. The labeling is not consistent (upper and lower cases mixed), and sometimes different symbols are used for the same quantity, for example the pore radius in Figures 7.5 to 7.8. The list of contents is quite inadequate.

However, despite these shortcomings the book can be recommended as a good survey of the literature in the area of oxometalates research. It is not very suitable for newcomers to the field.

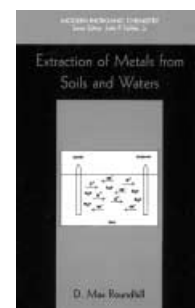
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Extraction of Metals from Soils and Waters. By *D. Max Roundhill*. (Series: Modern Inorganic Chemistry.) Kluwer Academic/Plenum Publishers, New York 2001. 375 pp., hardcover € 127.00.—ISBN 0-306-46722-4

With the publication of this book on the extraction of metals from soils and waters, at last we now have a work which reviews the current

state of research and development in this area from the viewpoint of inorganic and coordination chemistry. This third book by Max Roundhill in the *Modern Inorganic Chemistry*

series provides a thoroughly competent treatment which will serve the needs of both researchers and users of the methods. As well as having a logical and systematic structure, the text is written in an easily readable style so that the contents can be assimilated quickly. The clear arrangement of the material according to the different methods and heavy metals will ensure that the above



two groups of users can quickly find information on aspects of special interest. On one hand, by explaining the advantages and disadvantages of the various extraction methods it enables the user to make an informed choice, and also to choose the most suitable ligands, for example with regard to metal selectivity. The researcher, on the other hand, will be able to evaluate his or her own results (using different ligands or extraction methods) by comparing them with the results reported in the book. Thus, the author wisely decided to include not only methods that have already been tested in field trials, but also results from research on other interesting methods which are still only at the laboratory stage. Since there is such a vast amount of published work in this area, the literature references in the chapters can only show a small selection of it, but nevertheless they will allow the reader to go into these topics in greater depth. This is a very active field of research, as the need to clean up soils and waters polluted with heavy metals is becoming increasingly important, and very few established methods are yet available.

Five of the thirteen chapters are devoted to describing the most important methods. A 20-page chapter entitled "Phase-Transfer Extraction and Adsorption" explains basic principles (equilibria, aqueous two-phase systems, detergents, liquid membranes) and describes some important methods (ion exchange, polymer filtration, and adsorption on solid phases, polymers, or biopolymers). A chapter of 10 pages deals with soil washing and in situ stabilization, including electrochemical metal deposition by complex formation. A separate 10-page chapter is devoted to electrokinetic extraction, first explaining the methods then describing their application to the removal of ions and compounds of toxic metals (Cr, Cd, Cu, Pb, Hg, U).

Over 30 pages are devoted to the design of selective ligands, with detailed discussions of the advantages and limitations of various classes of multidentate ligands, macrocycles, and calixarenes, as well as ligands for extraction by supercritical carbon dioxide.

In an age when an increasing amount of research is interdisciplinary, the chapter on extraction of metals from soils and

waters by phytochemical and other biological agents is a valuable extension of the book's scope, especially as it shows the great potential of these approaches. The examples in this chapter are mainly limited to the use of plants and micro-organisms (including genetically modified strains) for extracting heavy metals from soil, probably to avoid unduly increasing the size of the book. Water treatment through absorption or uptake by algae, chitosan, and other types of biomass is only mentioned very briefly, and the choice of literature cited in this chapter appears to be not well-balanced.

The book's second main theme, the extraction of ions of toxic heavy metals (Hg, Pb, Cd, Cu, Cr, actinides, and lanthanides) and of other metals (Ag, Au, alkali metals, alkaline-earth metals), is treated in detail in six chapters. The arrangement of results according to ligand classes (monodentate ligands, chelating ligands subdivided according to donor atom types, macrocycles, supercritical carbon dioxide, etc.) makes it easy to compare efficiencies and to find individual ligands using the index. Clear structural formulas are given for crown ethers, their aza and thia analogues, and calixarenes. Information about the relationship between molecular structure and complex stability and/or selectivity includes quantitative data (K_{ex} or percent extraction) in some cases. The author also discusses some related questions, such as how heavy metals enter the soil, the forms in which they exist there, how they can then enter the food chain, and what remedies are available against toxic effects. For some of the ligands described in these chapters, problems such as the cost of synthesizing them or partial solubility in water make it doubtful whether they will ever be used for metal extraction, but despite that, the molecular design principles that give them their selectivity are of great interest. It is up to the reader seeking a solution to an extraction problem to decide which ligand might be suitable for scaling up from laboratory experiments to field tests, or what should be the structure of such a complexing agent. However, because of differences in the substrate material or matrix and in the required degree of selectivity, and the wide variety of possible ligands, the user must choose the method to suit the

specific problem. Up to now only a few preliminary results from field trials are available for selective macrocycles, but there are more for well-known chelating agents such as EDTA and NTA.

Selective complexing agents, column-packing materials, and extraction media for removal of Hg^{II} and Pb^{II} ions are described (20 pp. on each element), and related problems such as the removal of elemental mercury and analyzing samples for lead are also discussed. A section explaining that eating fairly large amounts of paper can cause Pb^{II} poisoning is of course very brief. Ligands for extracting Cd^{II} and Cu^{II} ions are also described (10 and 15 pp. respectively).

The extraction of silver and gold is also discussed because of the economic value of recovering them. An interesting aspect of this section is that new ligands could be an alternative to cyanide for metal winning. The 30-page chapter on lanthanides and actinides describes extraction and complexing methods, especially in the context of removing radioactive contamination.

A chapter of about ten pages discusses the design of ligands for binding to anions (mainly of chromium, also of selenium and technetium, but nothing on arsenic), and reports results on complex formation and extraction. There are also cross-references to other chapters in which methods are described with examples.

Over 30 pages are devoted to crown ethers, cryptands, and calixarenes that act selectively for alkali and alkaline-earth metal ions. These methods are not primarily of interest from the standpoint of extraction from soils, as it is normally not desired to remove these elements, except for the special cases of ^{137}Cs and ^{90}Sr . However, the chapter is very instructive with regard to selective ligand design and analytical aspects.

In almost every chapter, as well as chemical separation, analysis is also considered. Selective ligands can be used, in modified forms where necessary, for quantitative detection of heavy metals in soils. The last chapter, "Optical and Redox Sensors for Metal Ions" (50 pp.), deals specifically with that aspect. The author explains the mechanisms for generating an analytical signal from metal complexation, and describes the types of ligands to achieve this (chelating

agents, macrocycles, crown ethers, anion-selective ligands, etc.). The chapter ends with examples for particular metal ions and biological applications. Since almost every water-insoluble ligand can be used to make an ion-selective electrode, a discussion of potentiometric applications would of course be superfluous here.

The literature references mainly extend up to 1999, and in some cases to

2000 (including ACS Symposia, for example). As this is such an active area of research, it has only been possible to include a representative selection and to report the work of only some of the many groups. As well as describing many results of complexation studies, the book discusses their applications, thereby enabling chemists to relate their research to practical aspects. Users, on the other hand, will learn from this book that they

should not restrict their outlook to the few existing commercial processes, but should also seek advice from complexation chemists.

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