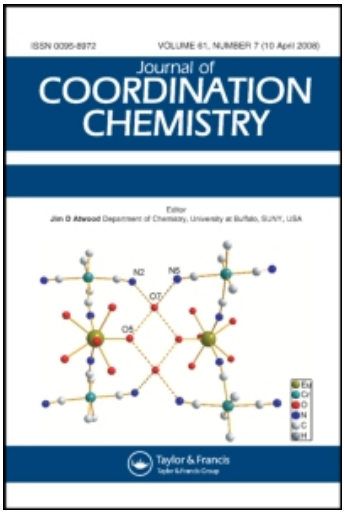

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A review of: "Metal Complexes in Aqueous Solution"

P. Caravan[a]
[a] Medicinal Inorganic Chemistry Group Department of Chemistry, University of British Columbia,

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BOOK REVIEW

Metal Complexes in Aqueous Solution
Arthur E. Martell and Robert D. Hancock

In the preface to their book, the authors state, 'Stability constants are fundamental to understanding the behavior of metal ions in aqueous solution.' Using thermodynamic arguments, Martell and Hancock go on to describe factors which influence metal complex stability and metal ion selectivity in aqueous solution. The first chapter is a fourteen page overview of an undergraduate coordination chemistry course which serves to remind the reader of such topics as the Hard/Soft Acid Base Principle, linear free energy relationships, coordination numbers, and ligand field effects. Chapter two examines factors affecting complexation of unidentate ligands. Here the role of solvent is examined by comparing protonation and complexation reactions in the gas phase with those in aqueous solution. Linear free energy relationships are used to delineate hard and soft metal ions and ligands, and the various donor types (O, N, S, *etc.*) are surveyed. Chapter three surveys chelating ligands, and involves discussions on optimal chelate ring size and the fusion of multiple chelate rings on the selectivity of a ligand for a given metal ion. Chapter four discusses macrocycles, their selectivity, and the origins of the macrocycle effect. Chapter five uses the principles discussed in Chapters 2–4 in the examination of metal complexes of medical interest, while Chapter six applies these principles to the role of metal ions in biology. The last chapter deals with the experimental determination of stability constants.

The strengths of this book lie in Chapters two through four. Equations and graphical relationships are provided for the prediction of stability constants. Neutral and anionic oxygen donors, saturated and unsaturated neutral nitrogen donors, and, to some extent, thiolato donors are discussed with respect to which metal ions they thermodynamically favor in aqueous solution. Here, the effect of six-membered chelate rings favoring smaller metal ions is explained. A strong argument is made for the role of inductive effects and how these compete with steric factors in the stability of a given complex. Good use is made of molecular mechanics arguments in examining steric effects and the

fusion of multiple chelate rings. A host of ligands are discussed ranging from flouride to binucleating macrocycles. In a book featuring so many comparisons between various metals, ligands, and stability constants, the work is exceptionally well presented. One rarely has to look beyond a page to find a drawing of the ligand being discussed. The figures are well annotated, again with ample use of chemical structures.

Martell and Hancock explain which donors and ligand topologies favor which metals and why they do so. Using the tenets presented, the book is a guide to ligand design for metal complexes in aqueous solution. In Chapter five, the authors discuss various metals of interest medicinally, either of a toxic, therapeutic, or diagnostic nature. The ligands used in medicinal inorganic chemistry are rationalized using the principles developed earlier in the book. A similar approach is taken in the following chapter where some examples of metal ions in biology are probed. Again the selectivity of a protein for, say, calcium over magnesium is explained on the basis of the coordination chemistry arguments made earlier in the book.

Many of the arguments put forth in this book have appeared previously in reviews by one or both of the authors, and as such, the bulk of the references are to the authors' work. However, salient reviews, books, and landmark papers are referred to in the introduction of new topics.

The sound arguments backed up by thermodynamic data are in a sense a limiting factor in this book. Little mention is made of donors such as thioethers and phosphines, or of 2nd and 3rd row transition elements, presumably because there exists little formation constant data to warrant their inclusion. In this respect, the ten pages (in the chapter on medicinal applications of metal complexes) devoted to technetium chemistry seem out of place; the other metals discussed in this chapter are scrutinized in terms of ligand design principles - which ligands are effective chelators of a given metal and why. In the same chapter, significant text (8 pages) is devoted to the author' work on Ga(III) and In(III) as diagnostic radiopharmaceuticals; aluminum, nickel, copper, the actinides, cadmium, lead, arsenic, and mercury altogether are given only six pages.

This book is remarkably free from errors, however there are a few confusing points. The discussion of associative and dissociative mechanisms on page 10 has the two mechanisms described as S_N1 and S_N2 in the text, *a* and *d* in Figure 1.8, and B and A in the caption to Figure 1.8. Two lines of text are repeated on pages 88 and 89, and the stability constants listed for EDTA in Table 3.5 are wrong.

Despite these biases, this book is to be recommeded. It is easy to read, clearly annotated, and well referenced. Its scope reaches beyond the aqueous

coordination chemist to anyone dealing with metal ions in aqueous media. Workers in nuclear medicine, pharmacology, biochemistry, soil sciences, or anyone working with metal ions in aqueous solution should find this book useful.

P. CARAVAN
Medicinal Inorganic Chemistry Group
Department of Chemistry
University of British Columbia