
CRITIQUE AND BIBLIOGRAPHY

Macrocyclic Chemistry: Current Trends and Future Perspectives,
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Macrocyclic compounds belong to the latest of the most important classes of organic reagents. Chemistry of macrocyclic compounds is being actively developed. Among the current trends responsible for the development of this field are the following: enhanced interest in reagents for anions and neutral compounds; a shift from simple macrocycles to more complex structures and, generally, supramolecular aggregates, including those with controllable structure and properties; a detailed knowledge of the nature of interactions; and a gradual change to the molecular design of reagents. The book under review fully reflects these trends.

The book includes 25 chapters, an appendix (colored figures of some chapters), and a subject index. Professor Karsten Gloe (Dresden Technical University, Germany) is the editor.

The first chapter (R.M. Izatt with coauthors) gives a brief review of the history of International Symposia on Macrocyclic Chemistry. Since 1977, 30 meetings have been organized (one of them was held in 1990 in Odessa (Soviet Union)). A special section was devoted to the IBC Award in Supramolecular Science and Technology and its recipients (in 2005, Professor Kenneth Raymond, who is well known, in particular, due to his studies on synthetic siderophores and reagents for binding oxo cations, was the latest who received this award).

Chapter 2 (O. Lukin and F. Vögtle) is devoted to topological complexes. The simplest examples are catenanes (compounds made of interlocking macrocycles) and rotaxanes (mechanically interlocked molecular architectures consisting of a dumbbell-shaped molecule threaded through a macrocycle or a ring-like molecule). A more complex example is provided by molecular knots (knotanes), whose molecular topology forms a knot. Synthetic approaches to constructing these assemblies, which can principally form a basis for so-called molecular machines, are discussed. Chapter 3 (C.A. Schalley et al.) also deals with this subject matter and mainly considers self-assembly and template strategies in the synthesis of macrocyclic aggregates.

Chapter 4 entitled “Recent Developments in the Synthesis and *d*-Block Chemistry of Linked Multi-Ring Macrocyclic Ligands” (L.F. Lindoy) is devoted to

reagents bearing several macrocyclic moieties linked to each other via bridges or a common central nucleus. Aza and azathia macrocycles are mainly considered. In Chapter 5 (M. Schröder and V. Lippolis), data on the synthesis and structural aspects of nitrile- and amino-functionalized pendant arm derivatives of 1,4,7-triazacyclononane are surveyed (mainly based on the studies by the authors). Chapter 6 (B. König and J. Svoboda) describes azamacrocyclic systems with grafted fluorophore groups, which are suitable for the determination of metal ions (for example, copper), and polymers containing azamacrocyclic complexes, which can extract nucleotides and related compounds from aqueous solutions. In Chapter 7, P.D. Beer and W.W.H. Wong survey their studies on supramolecular chemistry, in particular, bis-calix-quinone receptors for rubidium and cesium ions.

The subsequent five chapters are primarily devoted to the binding of anions. In Chapter 8 (R. Dickens and D. Parker), the coordination of anions to complexes of pendant derivatives of aza macrocycles is considered based on the data of NMR, fluorescence, and CD spectroscopy. Chapter 10 (S.J. Brooks and P.A. Gale) deals with the interactions of cyclic and open-chain 2-ami-dopyrrole derivatives with anions (halides, dihydrophosphate, etc.). Chapters 11 (K. Bowman-James with coworkers) and 12 (V. McKee and coauthors) are devoted to the binding of halide ions and oxo anions by protonated cryptands and their derivatives, respectively. Attention is focused on the stereochemistry of complexes. Chapter 9 (B.D. Smith) on salt and ion-pair recognition by ditopic macrocyclic receptors, which simultaneously bind a cation and an anion, seems most interesting. Macrocyclic compounds bearing a crown ether ring (binds alkali/alkaline-earth metal cations) and an isophthalimide unit (binds anions, in particular, chloride) belong to reagents of the main class.

Chapter 13 (E. Luboch et al.) surveys published data on cyclodextrin combinations with aza compounds (dyes, diazonium salts, etc.). Chapter 14 (V. Balzani and coauthors) is devoted to complexes of bivalent ruthenium and bivalent osmium with a polyphenylene macrocycle bearing a bipyridyl unit (photophysical and electrochemical properties were studied). Chapter 15 (O.A. Fedorova, E.N. Ushakov, V.V. Fedorov,

Yu.P. Strokach and S.P. Gromov) surveys their studies of macrocyclic systems with photoswitchable functions based on photochromic crown ethers. Three classes of such systems are considered. In the first case (crown ethers with an added styryl dye fragment), *cis-trans* isomerization occurs under the action of light followed by a change in the conformation of the molecule and, as a consequence the accessibility of the peripheral coordination-active groups; as a result, the complexation properties of the reagent change. The second case covers the occurrence of a [2+2]-photocycloaddition reaction with the linking of two macrocyclic ligands in a bis metal complex to form a new molecule. The third case includes photoinduced switching with an electrocyclic reaction.

Chapter 16 (G.W. Gokel with coauthors) deals with the use of crown ethers and their derivatives as model systems for studying biological processes; in particular, artificial ion channels are considered. Chapter 17 (A.D. Hamilton with coauthors) is devoted to the synthesis of tetraphenylporphyrin derivatives bearing amino acid/peptide substituents in peripheral phenyl rings and to their binding to cytochrome *c* (here, the macrocycle serves as a platform for substituents that are responsible for binding).

Chapter 18 is entitled "Supramolecular Complexes with Macrocycles: Surprises and Insights" (H.-J. Schneider). This short chapter considers a number of cases in which a structural/thermodynamic interpretation of the effects observed in the stability of host-guest complexes is not obvious (or an obvious interpretation is incorrect). For example, the problem of the comparative roles of a hydrophobic effect and van der Waals interactions in the association of lipophilic particles in an aqueous medium is considered. Chapter 19 entitled "Calorimetry: An Indispensable Tool in the Design of Molecular Hosts" (F.P. Schmidtchen) specifies the range of problems that can be solved in host-guest systems using calorimetry. The following two examples are considered in detail: a study of the solvent contribution to the thermodynamics of the association of cyclodextrin with camphor in water (the contribution is quite significant!) and a study of the interaction of a substituted guanidinium cation with oxo anions (a typical binding motif in naturally occurring and synthetic systems).

Chapter 20 (P. Comba and B. Martin) gives a brief review of theoretical methods for analyzing the structure and stability of macrocyclic complexes and exemplifies their use. In accordance with the interests of the authors, attention is focused on the molecular mechanics method and the coordination aza reagent compounds. The next chapter, Chapter 21 entitled "Simulations of the Dynamics of 18-Crown-6 and Its Complexes: From the Gas Phase to Aqueous Interfaces with SC-CO₂ and a Room-Temperature Ionic Liquid" (G. Wipff and coworkers), is also devoted to a theoretic-

cal analysis. Molecular mechanics calculations are presented. It is of interest that an important section deals with the simulation of strontium extraction with 18-crown-6 into an ionic liquid, butylmethylimidazolium hexafluorophosphate.

Chapter 22 entitled "Application of Macrocyclic Ligands to Analytical Chromatography" (J.D. Lamb and J.S. Gardner) is of direct interest to analytical chemists. This rather brief review (15 pages) with 107 references is an introduction; of macrocyclic compounds, crown ethers are mainly considered. This chapter is a good starting point for familiarizing oneself with this research field because of a considerable number of references to recent publications, monographs, and reviews. Chapter 23 entitled "Ligand Design for Base Metal Recovery" (P.A. Tasker and V. Gasperov) is also of interest. This short chapter deals with the use of the concepts of preorganization and supramolecular aggregation, which appeared in the context of macrocyclic compounds, rather than macrocycles (the authors point out that cyclic reagents are not in current use for economical reasons and they will be hardly used in hydrometallurgy on a large scale). Phenomena such as the formation of pseudomacrocycles from two salicylaldehyde molecules (due to hydrogen bonds; this was observed in both free reagents and complexes) and the dimerization of alkylphosphonic acids are discussed and analyzed from the standpoint of the efficiency and selectivity of metal extraction. In Chapter 24, which is entitled "Use of Macrocycles in Nuclear-Waste Cleanup: A Real-World Application of a Calixcrown in Cesium Separation Technology," B.A. Moyer with coauthors describe in detail the caustic-side solvent extraction (CSSX) process for the separation of cesium from aqueous alkaline solutions (with the use of calyx[4]arene-bis(4-*tert*-octylbenzocrown-6)). The class of calixcrown ethers was proposed by European researchers (Ungaro, Vicens, et al.). An extraction technology, as applied to a particular problem of the removal of radioactive cesium (Savanna River, Hanford), was developed at the Oak Ridge National Laboratory in the United States. The efficiency of cesium extraction is higher than that with ordinary crown ethers by a factor of 100–1000; selectivity is also high: extraction can be performed in the presence of 10⁴- to 10⁶-fold amounts of sodium.

Chapter 25 entitled "Texaphyrin Conjugates: Progress toward Second Generation Diagnostic and Therapeutic Agents" (J.L. Sessler and coworkers) is devoted to texaphyrins, a class of aza macrocycles (three pyrrole and two imine nitrogen atoms in a conjugated 17-membered ring; the name is indicative of a similarity to porphyrins and of Texas origin), which are actively studied by the group of Professor Sessler at the University of Texas in Austin. These ligands afford stable complexes with rare-earth elements. For yet unknown reasons, these complexes are concentrated in

tumor tissues in the body. Because of this, it is evident that their conjugates with cytotoxic agents, fluorophores, etc., are clinically promising.

In general, the book under review is a typical collection of articles. From chapter to chapter, the style of writing varies from a monographic style of reviews to a detailed journal style; the book contains a great number of self-reviews. The book is primarily useful to specialists in the chemistry of macrocyclic compounds and in

the chemistry of host-guest complexes. It is likely that Chapters 8–12 and 22–24¹ will be most interesting for the broad masses of analytical and inorganic chemists.

I. V. Pletnev

¹In this context, the following Russian monograph should be mentioned: *Makrotsiklicheskie soedineniya v analiticheskoi khimii* (Macrocyclic Compounds in Analytical Chemistry), Zolotov, Yu.A. and Kuz'min, N.M., Eds., Moscow: Nauka, 1993.