Book Reviews

F. Vögtle (ed.): *Host-Guest Complex Chemistry* (Topics in Current Chemistry Vols. 98 and 101), Springer-Verlag, Berlin, Heidelberg, New York, 1981 and 1982.

These two volumes of 'Topics in Current Chemistry' contain seven reviews describing some major advances in host-guest complex chemistry that have taken place since the middle seventies. The primary interest is concentrated on the exploration of possible applications of crown-type macrocycles as model compounds in reactions of stereoselective complexation, ion transport and molecular catalysis. The individual reports are preceded by an excellent introductory overview by E. Weber and F. Vögtle in which the variety of novel crown-based ligand systems is illustrated and classified. A brief survey of the most important properties of these ligands is also included.

The stereochemistry of host-guest complexes is the main subject in three contributions to the series. D.J. Cram and K.N. Trueblood, referring mostly to their own research work, give a good and solid account of the structures and complexing properties exhibited by synthetic macrocyclic hosts. The ligands involved, crown ethers and hemispherands binding molecular guests, and spherands complexing metal cations, are characterized by a varying degree of conformational flexibility. Features of conformational reorganization revealed by these ligands upon complexation as well as geometrical relationships between the binding sites are thus referred to in more detail. Of particular interest is the description of the molecular model development process and the corresponding correlations between structure and free energy of complexation which reflect on the stabilities and selectivities of the various systems.

The association of crown-type hosts with uncharged guest molecules and with guest anions is reviewed by F. Vögtle, H. Sieger and W.M Müller. This chapter provides an exhaustive survey of the types of structures and their host-guest stoichiometries that have been found in solution as well as in the solid phase. There is an emphasis on the characterization of complexes involving flexible open-chain ligands in addition to those formed by monocyclic crowns. The binding of anions as guest particles by macroheterocyclic species, which is still at the initial stages of research, is reviewed here for the first time.

A complementary discussion of complexes between ionophores and metal ions is presented by R. Hilgenfeld and W. Saenger. This contribution is the largest in the series. It is devoted to the stereochemistry of both natural and synthetic ionophores, including depsipeptides, macrotetrolides, polyether antibiotics, macrocyclic and macropolycyclic crowns, and open-chain polyethers. Bicomponent as well as multicomponent complexes are described. There are extensive tables of structural data accompanied by a large number of illustrations and references, reflecting a reasonably complete coverage of the literature to 1981.

The remaining chapters cover very varied ground. The potential use of macrocyclic ligands in enantioselective reactions is critically discussed by R.M. Kellogg. Most of the examples given in this chapter include crown ether macrocycles which exhibit catalytic activity in bond-forming and bond-breaking reactions. The resemblance to protease and hydrogenase activity makes these systems suitable bioorganic models. It is emphasized, however, that the good complexing ability of the crowns is usually associated with a slow kinetics of decomplexa-

tion. As a conclusion, the author states that much chemistry still remains to be done in order to develop functionalized ligands which could act truly as an enzymatic catalyst.

The analytical applications of monocyclic crowns and polycyclic cryptands are summarized concisely by E. Blasius and K. P. Janzen. These are divided into separation methods (e.g., extractions and chromatography) and determination methods (mainly electrochemical). The separation of cations, anions and optically active organic compounds, mostly by polymeric cyclic polyethers, is discussed in a somewhat technical manner. The application of cyclic polyethers as components of ion-sensitive electrodes is also mentioned.

The last two chapters are not really confined to crown type host-guest interactions, as has been indicated by the Editor in the Foreword. In fact, G. R. Painter and B. C. Pressman discuss mostly other ionophores and their ability to catalyze transport modes in membranes. Most attention is drawn to carboxylic ionophores, their conformational dynamics in various media, and their interactions with phospholipid membranes. The wide use of physical methods in the detection (and interpretation) of concentrations, conformational variations, binding interactions, and transport rates is demonstrated. It is noteworthy that the authors deal also with biological/pharmacological applications of some natural and synthetic ionophores and elucidation of the transport mechanism. Relevant examples of Na^+, K^+ and H^+ ion exchange across membranes are provided.

The contribution of F. Montanari, D. Landini and F. Rolla on phase-transfer catalysis, as presented, is rather weakly linked to the general subject treated in this series. The authors preferred to devote a major part of their chapter to the fundamentals of phase-transfer catalysis and to discuss many classical catalytic systems (such as quaternary salts) other than crown type macrocycles. The latter are relatively more expensive and proved to be significantly useful only in solid-liquid phase transfer. Several representative applications of phase-transfer catalysis have been summarized, but only a few of them are associated with macrocyclic systems.

The two volumes contain a large wealth of material, an enormous number of references, excellent figures and are also well produced and easy to read. On the negative side it is clear, however, that they provide a somewhat imbalanced representation of the subject, and do not cover the entire field. Indeed, many important aspects of host-guest chemistry (such as for example: thermodynamic studies, synthetic routes and cryptate chemistry) have been omitted or dealt with in insufficient depth. Nevertheless, this publication can be strongly recommended, not only to those who are directly involved in host-guest chemistry and seek specific information, but also to those who for any reason may have a general interest in this exciting and promising field of research.

ISRAEL GOLDBERG

J. Szejtli: *Cyclodextrins and their Inclusion Complexes*, Akademiai Kiado, Budapest, 1982, $ 30.

If starch is degraded by a certain class of amylases, cyclodextrins, also called cycloamyloses, are formed. They consist of cyclic oligosaccharides containing six to eight $\alpha(1,4)$-linked glucoses and have an annular structure with a 5 to 8 Å wide central cavity. Because of this particular geometry, the cyclodextrins are able to form inclusion complexes with guest molecules of appropriate size not only in the solid state but also in solution. Therefore,

cyclodextrins have found interest of an academic as well as of a practical nature. Whereas former reviews (e.g., *Cyclodextrin Chemistry* by Bender and Komiyama, Springer-Verlag, 1978) focused on the cyclodextrins' chemical and physical properties, the present book also encompasses possible and already realized practical applications in industry and pharmacy and therefore is the most complete review on cyclodextrins that is presently available.

The literature is covered up to 1979 (although the author has put in a few of his own papers up to 1981) and is classified in several individual chapters dealing with the chemistry and preparation of cyclodextrins, their toxicology and biochemistry; derivatized cyclodextrins, including polymerized cyclodextrins which can be used in column chromatography, are treated only briefly, since Bender and Komiyama have devoted a whole book to this topic; preparation of inclusion compounds of cyclodextrins, their physical and chemical properties; catalytic effects of cyclodextrins and their uses as model enzymes; cyclodextrin-drug complexes and their potential pharmacological application; cyclodextrins in the food and chemical industries. In total, a picture emerges that gives insight into the diverse phenomena to be studied academically with cyclodextrins and into their possible uses in everyday life. The latter might become of immediate interest because, as Professor Szejtli outlines in the Preface, the price of cyclodextrins has dropped by two orders of magnitude during the past seven years and might decrease even further, especially if industrial applications of cyclodextrins guarantee mass production.

Speaking of prices, $ 30 for this book is well spent. The book is recommended strongly to all those doing research in the field of inclusion phenomena, to pharmacologically interested people wanting to microencapsulate unstable or insoluble drugs to improve their handling properties, to those involved in chromatographic separation of different molecules, and to those working in the food, pesticide and herbicide industries.

WOLFRAM SAENGER

M. Dobler, *'Ionophores and their Structures'*. John Wiley, New York, Chichester, Brisbane, Toronto, 1981, 379 pp., £50.50.

Ionophores can be characterized as receptors which form stable, lipophilic complexes with charged hydrophilic species such as Na^+, K^+, Ca^{2+} etc., and thus are able to transport them into lipophilic phases, for example across natural or artificial membranes. According to this general definition, molecules as different as the natural antibiotic valinomycin and the synthetic linear polyethers (podands) belong to this group. In the past two decades, a wealth of information has become available on ionophore structures and functions which Dr. Dobler has gathered and presented in this well-organized book.

As in many other cases, it was mainly X-ray diffraction experiments (among these Dobler's own work on nonactin and 18-crown-6 complexes) that provided the most accurate information on ionophore structures. Consequently, the book mainly considers results obtained from X-ray studies although investigations of solution conformations are referred to as well.

In two introductory chapters the different types of ionophores are described and a brief survey of techniques to investigate their properties is given. Chapter 3 is devoted to the biological action of these compounds whereas Chapter 4 deals with the application of synthetic ionophores such as crown ethers in organic chemistry as reagents influencing the rate and stereochemistry of reactions.

Chapters 6 to 9 constitute the main part of the book and describe the spatial structures of ionophores, covering the literature until 1979. These structures are not simply reported one after the other but are examined critically. Careful comparisons between ligand conformations in both the complexed and the free state are given and in some cases the author attempts to deduce a possible mechanism of ion inclusion by the host molecule. Chapter 6 gives an excellent summary of the structural information available on cyclic depsipeptide antibiotics such as valinomycin and the enniatins as well as on the nactins (macrotetrolides). The next chapter deals in some length with the carboxylic polyether antibiotics. These are open-chain ligands which wrap around the metal ion and are held in this circular conformation by head-to-tail hydrogen bonds. Chapter 8 summarizes the structures of synthetic ionophores such as cyclic crown ethers, open-chain polyethers (podands) and cryptands and their cation complexes. A paragraph is devoted to chirality recognizing hosts, e.g., Cram's binaphthyl polyethers.

Some linear peptides ('quasiionophores') such as the gramicidins A, B, and C and alamethicin do not act as ion carriers but form transmembrane channels across which alkali metal ions can migrate. The few structural results which have been published on these antibiotics are highlighted (among others) in Chapter 9, where – one of the very few errors in this book – a cyclic structural formula is given for alamethicin which was shown to be incorrect about five years ago.

The presentation of X-ray crystallographic results is done in a uniform manner: Stereoscopic ball-and-stick drawings produced by the computer program PLUTO are used throughout the book which makes structures easily comparable. Maybe some space-filling plots would have been useful to demonstrate the fit between host (ionophore) and guest (cation) entities. Another minor criticism is that many structural formulas are depicted in the appendix only, so that one has to look these up quite often during reading.

In a second appendix, orthogonal coordinates for most of the structures reported are given. This is very useful for non-crystallographers such as research workers dealing with conformational energy calculations, but also for crystallographers not utilizing the Cambridge Crystallographic Data Bank.

In summary, this is a book which will be highly welcomed by structural chemists working in the field. Moreover, it is warmly recommended to those utilizing the unique properties of ionophores for biological and chemical applications for it gives a comprehensive overview of the structural foundations of ionophore action. The enormous number of illustrations and tables even justifies the price of £50.50.

ROLF HILGENFELD