

Topics in Current Chemistry

121

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Alkaline Earth Metal Ion
Selective Chromogenic Reagents

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Ion Transport by Photofunctional
Crown Ethers

J. Smid and R. Sinta
Macroheterocyclic Ligands on Polymers

Th. A. Kaden
Synthesis and Metal Complexes of
Aza-Macrocycles with Pendant Arms
having Additional Ligating Groups

J. E. Baldwin and P. Perlmutter
Bridged, Capped and Fenced Porphyrins



Host Guest Complex Chemistry III

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Host Guest Complex Chemistry III

Editors: F. Vögtle, E. Weber

With Contributions by

J. E. Baldwin, Th. A. Kaden, O. Manabe, P. Perlmutter,
S. Shinkai, R. Sinta, J. Smid, M. Takagi,
Y. Takeda, K. Ueno

With 72 Figures and 29 Tables



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Topics in Current Chemistry

Fortschritte der Chemischen Forschung

Managing Editor: F. L. Boschke



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Preface

Since C. J. Pedersen reported the synthesis of the first crown ethers in 1967, interest in organic multidentate ligands has continually increased. The research concerning these compounds is broad, ranging from synthesis of new ligand topologies to investigations of selective binding properties and their application in the catalysis of synthetic organic reactions to analytical separation and determination problems. This volume is the third in a series, presenting a selection of contributions in the interesting field of modern coordination chemistry with organic ligands. At present, the functional facet of neutral ligands is perhaps the most exciting one. Therefore the overall contents of the various chapters is "to let the crown compounds work".

Chapter 1, by Y. Takeda, presents a detailed introduction of the solvent extraction of metal ions by crown compounds. Fundamental physical equilibria, which are helpful in understanding extraction processes are explained, and the various factors affecting the extent of ion extraction are discussed. Examples of analytical applications (separation analysis, colorimetric determination) of this technique round up the picture.

Chapter 2, by M. Takagi and K. Ueno, shows crown compounds functioning as alkali and alkaline earth metal ion selective chromogenic reagents. This report deals with recent developments in the synthesis of crown derivatives, which have chromophoric functional groups within its molecular skeleton (crown ether dyes). These compounds are designed to bring about specific colour changes on the interaction with certain alkali/alkaline earth metal ions, thus being able to serve as probes of photometric reagents for these metal ions. The utility of modified types of indicator systems in the fluorescence analysis of ion concentration is also demonstrated, showing the idea of chromoionophores to be realized in a broad sense.

Chapter 3, by S. Shinkai and O. Manabe, offers a review over the fascinating field of coupled ion transport. Artificial membrane systems affected by an energy switch of light, a pH-antenna, a redox-couple and other types of responsive functionalities introduced into a crown carrier are discussed "at work". Studies on liposomal membranes are also included. The scope of the principle of responsive functionality control by modified crown compounds shows a new entry into enzyme mimickry in respect to certain coupled ion/electron transport processes.

Chapter 4, by J. Smid and R. Sinta, deals with the synthesis and the binding properties of polymeric crown/cryptand ligands (linear polymeric and those anchored to insoluble supports). Extensive information on the complexation behaviour in

aqueous and nonaqueous media is given. The effect of variables in polymer structure is analyzed and applications in ion transport, exchange resin chromatography and polycrown catalysis are demonstrated.

Chapter 5, by T. A. Kaden, describes an interesting new class of ligands which combine structural characteristics of a macrocyclic oligoaza ligand with specific properties of coordinating flexible side chains. Insight into the relations between reactivity and structure of the pendant functional groups and of the bound metal ion is given. The different complex geometries in respect to the functional group appendages (axial coordination) and possible applications regarding enzyme analogy are also discussed.

The concluding *chapter 6*, by J. E. Baldwin and P. Perlmutter, reviews the chemistry of diverse metalloporphyrin derivatives, which over the last decade have become known as "bridged, capped and fenced porphyrins". The article is divided into sections dealing with synthetic models for haemoglobin, myoglobin, cytochrome P-450, cytochrome *c* oxidase. Each section includes a brief description of the natural system with the properties, which should be considered in a reliable model.

As a general conclusion these contributions demonstrate that the crown chemistry has reached a level beyond merely synthesizing ligands and the formation of ordinary crown complexes, but is concerned with the sophisticated functionalization of crown compounds in terms of styling new controlling processes and regulation systems in response to a functionality couple. The spreading of these principles into different fields of application (dye stuffs, drugs, micelles, enzyme models, membrane ionophores etc.) are coming off broadly.

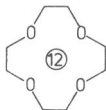
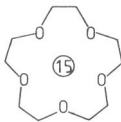
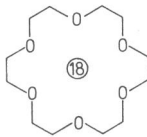
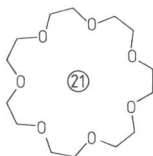
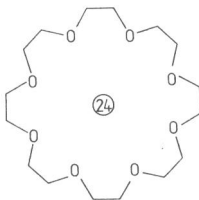
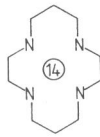
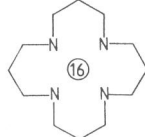
This book therefore aims at researchers and students in organic, physical, analytical, and inorganic chemistry, but should also be of interest for many from the biological, physiological and physiochemical fields.

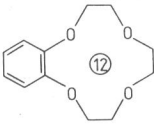
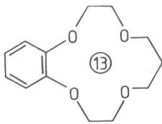
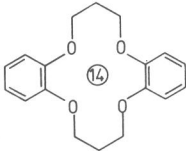

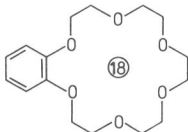
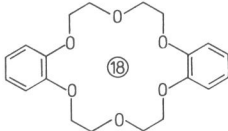
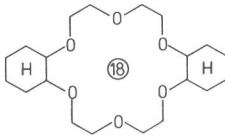
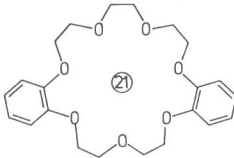
The editors wish to acknowledge their indebtedness to all who have helped in bringing this book to completion.

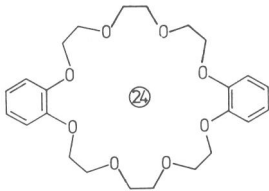
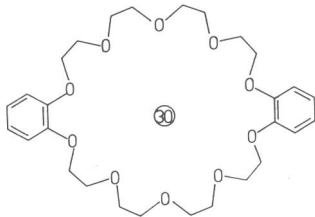

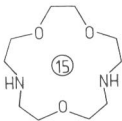
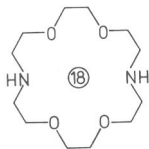
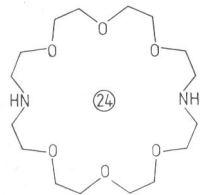
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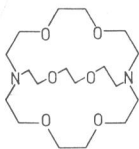
F. Vögtle, E. Weber

List of constitutional formulae of crown compounds and of their notations/abbreviations frequently used in this volume^a

Formula	Notation	Abbreviation
	[12] crown - 4	12C4
	[15] crown - 5	15C5
	[18] crown - 6	18C6
	[21] crown - 7	21C7
	[24] crown - 8	24C8
	Tetraaza [14] coronand - 4	TA14C4
	Tetraaza [16] coronand - 4	TA16C4

Formula	Notation	Abbreviation
	Benzo[12]crown-4	B12C4
	Benzo[13]crown-4	B13C4
	Dibenzo[14]crown-4	DB14C4
	Benzo[15]crown-5	B15C5
	Benzo[18]crown-6	B18C6
	Dibenzo[18]crown-6	DB18C6
	Dicyclohexano[18]crown-6	DCH18C6
	Dibenzo[21]crown-7	DB21C7

Formula	Notation	Abbreviation
	Dibenzo[24]crown-8	DB24C8
	Dibenzo[30]crown-10	DB30C10
	Monoaza[15]coronand-5	MA15C5
	Diaza[15]coronand-5	DA15C5
	Diaza[18]coronand-6	DA18C6
	Diaza[24]coronand-8	DA24C8

Formula	Notation	Abbreviation
	Cryptand [2.2.2]	[2.2.2]

^a For more detailed information on crown/cryptand nomenclature see ("Crown-Type Compounds — An Introductory Overview") Weber, E., Vögtle, F.: *Top. Curr. Chem.* 98, 1 (1981); sect. 2 and 3.1.

Host Guest Complex Chemistry I

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1981. 80 figures, 25 tables. VII, 197 pages

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Contents/Information:

E. Weber, F. Vögtle: Crown Type Compounds – An Introductory Overview. The scientific and practical interest in coronands (crown ethers), cryptands and podands as complexing agents for cations as well as for anions and neutral low molecular species is undeniable. The chemistry of crown compounds is expanding steadily, to the point where over 200 original papers dealing with crown chemistry appeared in 1980 alone. To help their colleagues keep abreast of the continuous synthesis of new crown ether properties of their applications, the authors of this article provide a critical review of the current status of research in the field. New molecules with crown ether properties are constantly synthesized and new applications discovered. (80 ref.).

D. J. Cram, K. N. Trueblood: Concept, Structure, and Binding in Complexation. This paper is concerned with applications of the techniques of organic chemistry and crystallography to the study of structural recognition in complexation between partners, at least one of which is a designed synthetic organic compound. (61 ref.).

F. Vögtle, H. Sieger, W. M. Müller: Complexation of Uncharged Molecules and Anions by Crown-Type Host Molecules. The emphasis in this report lies on new possibilities of inclusion with the smaller unimolecular cavities of coronands (crown compounds), cryptands, catapinands and podands (open chain crown-type compounds). The neutral molecular complexes of these compounds are to be understood as adducts with small molecular particles; these adducts are not held together primarily by electrostatic (ionic) interactions. (130 ref.).

E. Blasius, K.-P. Janzen: Analytical Applications of Crown Compounds and Cryptands. Crown compounds and cryptands have widely been used in analytical chemistry. Variable ring sizes, the type, the number, and the position of the donor atoms in the ether ring permit a selective adaptation to a certain cation.

The reference for a certain salt is expressed by the value of the selectivity constant, i.e. the ratio between two stability constants. When selectivity constants are high, separations and determinations of cations and anions are possible. (99 ref.).

Host Guest Complex Chemistry II

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1982. 140 figures, 40 tables. VIII, 203 pages

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Contents/Information:

R. Hilgenfeld, W. Saenger: Structural Chemistry of Natural and Synthetic Ionophores and Their Complexes with Cations. The antibiotics nigericin and lasalocid as first representatives of the naturally occurring ionophores were isolated in 1951 from streptomyces cultures. In the late sixties the function of these compounds as complexing and transporting agents for alkali metal ions was established, where upon they attracted the attention of numerous investigators. The numerous details learned about their structures, complex formation and physiological activity since that time are reviewed in this article.

G. R. Painter, B. C. Pressman: Dynamic Aspects of Ionophore Mediated Membrane Transport. The dynamic molecular properties underlying the transport activity of ionophores are discussed with emphasis on the effects of membrane microenvironment on the transport mechanism. Preliminary results indicate that membranes of differing phospholipid composition show differential affinities for a given ionophore as well as differential cation transport efficiencies for each equivalent of ionophore bound.

R. M. Kellogg: Bioorganic Modelling, Stereoselective Reactions with Chiral Neutral Ligand Complexes as Model Systems for Enzyme Catalysis. The material accumulated in this review leads to conclusion that crown (or cryptate) systems in particular offer special advantages in bioorganic modelling because such compounds can – like enzyme – complex a potential substrate. On the basis of simple binding considerations, coupled with an analysis of steric interactions, accurate predictions of the stereochemistry of the complex can be made. Potential areas of applications of chiral crown ether (or cryptate) ligand systems in bioorganic modelling lie in, for example, the formation of carbon-carbon bonds, development of oxidative processes, synthesis of metal complexes with oxygenase activity, and the development of compounds with group transfer abilities.

F. Montanari, D. Landini, F. Rolla: Phase-Transfer Catalyzed Reactions. A number of organic reactions proceed through the attack of anions on the substrate or through primary formation of reactive anionic species. The acceleration of such reactions, thus allowing them to be run under mild conditions, has been a traditional goal in organic chemistry. The observation that nearly unsolvated anions and/or interacting sparingly with neighbouring cations are highly reactive suggested a solution of this problem. The introduction of dipolar aprotic solvents and the discovery of macrocyclic (crown ethers) and macrobicyclic polyethers (cryptands) represent some of the more significant steps. A new general technique was developed: phase-transfer catalysis.



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Volume 14: W. P. Weber

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Volume 13: G. W. Gokel, S. H. Korzeniowski

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Volume 11

New Syntheses with Carbon Monoxide

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1980. 118 figures, 127 tables. XIV, 465 pages
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The Solvent Extraction of Metal Ions by Crown Compounds

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1 Introduction

Solvent extraction is a convenient and useful method in solution and analytical chemistry. It can be employed to concentrate and separate metal ions, and to determine stoichiometries and stabilities of complexes extracted into an organic phase. It thus makes sense to use solvent extraction for studying the complexing ability of crown ethers (including cryptands) toward metal ions. Crown ethers consist of hydrophilic cavities and hydrophobic exteriors, and form stable complexes particularly with alkali and alkaline earth metal ions by holding the ions in the central cavity. To date, numerous papers report on metal ion binding properties of newly synthesized crown ethers determined by solvent extraction.

In general, the selectivity of crown ethers for metal ions in solvent extraction systems largely depends on the relation between the size of the metal ion and the cavity of the crown ether; in other words, the metal ion which fits the crown ether cavity best is the most extractable. Extraction equilibrium constants and distribution ratios are very important for analysis as they are a measure of extractability of a metal ion. Since extraction equilibrium is a result of several constituent equilibria, stability of a crown ether complex with a metal ion in an aqueous solution is not always a dominant factor in determining the magnitude of the extraction equilibrium constant. Therefore, it is important to analyze the extraction equilibrium by means of the constituent equilibria, and furthermore, to investigate the influence of each of the constituent equilibria on the extraction equilibrium. This would give a valuable hint for the molecular design of new crown ethers with high extraction-selectivity for a given metal ion.

In order to compare the relative complexing powers of various crown ethers for alkali metal ions, Pedersen¹⁾ was first to employ the solvent extraction method. He reported that alkali metal ions which more optimally fit the crown ether cavity are more extractable. Frensdorff²⁾ elaborately studied the extraction of sodium and potassium picrates with dicyclohexano[18]crown-6 (DCH18C6)¹ A and B, and dibenzo[18]crown-6 (DB18C6). These experiments established the basic equilibria of the extraction process. In order to clarify the role of crown ethers in the extraction process, he analyzed the overall extraction equilibrium by studying three of the constituent equilibria: complex formation in the aqueous phase and distribution of the uncomplexed and the complexed crown ether.

2 Equilibrium for Extraction of Metal Ions by Crown Ethers

Extraction equilibrium between an aqueous phase of a metal ion (M^{m+}), a counter anion (A^-), and an organic phase of a crown ether (L), may be represented by the following equation:



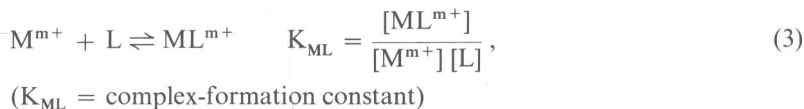
1 A list of the frequently used notations and their explanation are given on page XI

where K_{ex} is the extraction equilibrium constant; MLA_m designates as ion pair between a crown ether complex with the methyl ion (ML^{m+}) and the counter anion; subscript "o" and the lack of subscript denote an organic and an aqueous phase, respectively; square brackets indicate molar concentrations. The extraction equilibrium is considered to consist of the following constituent equilibria:

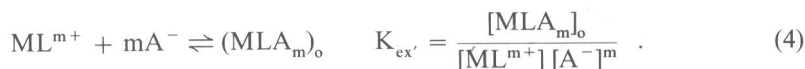
— distribution of the free crown ether between the two phases:



— complexation reaction of the crown ether with the metal ion in the aqueous phase:



— ion-pair extraction of the crown ether-metal ion complex with the counter anion:



If a nonpolar solvent is used as an organic phase, dissociation of the ion pair MLA_m in the organic phase will be negligible:

$$K_{\text{ex}} = D_L^{-1} K_{\text{ML}} K_{\text{ex}}'. \quad (5)$$

The all-activity coefficients of the chemical species mentioned here are assumed as unity. However, when the concentrations of the metal ions and/or the counter anions in the aqueous phase are high, it is necessary to take into account the activity coefficients of the ions.

The distribution ratio of the metal ion can be defined as follows:

$$D_M = \frac{[\text{M}]_{o,t}}{[\text{M}]_t},$$

and calculated from the experimental data where $[\text{M}]_{o,t}$ and $[\text{M}]_t$ are total metal concentrations in the organic and aqueous phases, respectively. Assuming that every ion-pair formation is negligible in the aqueous phase because of the high dielectric constant of water we arrive at:

$$D_M = \frac{[\text{MLA}_m]_o}{[\text{M}^{m+}] + [\text{ML}^{m+}]}. \quad (6)$$

The $[\text{MLA}_m]_o$ value can be obtained experimentally. In the case of $[\text{M}^{m+}] \gg [\text{ML}^{m+}]$ Eq. 6 becomes:

$$D_M = K_{\text{ex}} [\text{A}^-]^m [\text{L}]_o. \quad (7)$$