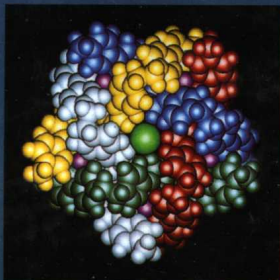


SUPRAMOLECULAR CHEMISTRY OF ANIONS



Edited by
Antonio Bianchi
Kristin Bowman-James
Enrique García-España

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and

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 **WILEY-VCH**

New York • Chichester • Weinheim • Brisbane • Singapore • Toronto

About the Front Cover Design

Crystal structure of the chloride inclusion complex of the circular double helicate formed with iron(II) and a *iris*-bipyridine ligand.

From B. Hasenknopf, J.-M. Lehn, B. O. Kneisel, G. Baum, and D. Fenske, *Angew. Chem., Int. Ed. Engl.* **35**, 1838 (1996).

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Published simultaneously in Canada.

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Library of Congress Cataloging in Publication Data:

The supramolecular chemistry of anions / [edited by] Antonio Bianchi,
Kristin Bowman-James, Enrique García-España.

p. cm.

Includes bibliographical references and index.

ISBN 0-471-18622-8 (alk. paper)

1. Anions 2. Macromolecules. 3. Coordination compounds.

I. Bianchi, Antonio, 1956– . II. Bowman-James, Kristin, 1946–

III. García-España, Enrique.

QD474.S9525 1997

541.2'26—dc21

Printed in the United States of America

10 9 8 7 6 5 4 3 2 1

FOREWORD

Anion complexation was unrecognized until rather recently, while cation binding has been extensively studied for about a century. Although I was convinced from the start that there was a whole field to explore, the proposal made in the late 1970s (see *Acc. Chem. Res.* **11**, 49, 1978; *Pure Appl. Chem.* **50**, 871, 1978) that anion coordination chemistry was an identifiable and bona fide area of investigation was not accepted readily. But over the years, things have changed drastically. Thanks to the work of an increasing number of investigators, a body of results on anion binding, recognition, and transport, as well as on supramolecular catalysis involving anionic species, has accumulated. A variety of anion receptor molecules incorporating different types of anion binding sites has been devised, and their properties have been investigated. The recognition of anionic substrates of different shapes and charges has been achieved, as well as the catalytic transformation of substrates within supramolecular entities.

In harmony with the important role played by anionic species both in chemistry and in biology, anion coordination chemistry has become an established new domain of a generalized coordination chemistry. The field has been reviewed recently on several occasions. The present volume indicates that it has reached the status of a mature area of investigation. It provides a thorough overview of what has been realized and should inspire further developments. Indeed, this is just the start—anion coordination chemistry is a young field, wide open to future progress.

I wish to congratulate the editors and the authors for producing this high-level, very timely work, which should be of great value to chemists and biologists alike. It will help to further the cause and broaden the scope of anion coordination chemistry.

JEAN-MARIE LEHN

PREFACE

Supramolecular chemistry has developed in the past decades as a borderline scientific field destined to fill part of the conceptual gap between chemistry, physics, and biology. This chemistry, which bases its evolution in the Paul Ehrlich receptor concept and on the ideas of Alfred Werner on coordination, can be understood as an extended coordination chemistry in which the objects of coordination are not just metal ions but also organic cations, neutral organic or inorganic species, and anionic species of various types. Within this chemistry, the *supramolecular chemistry of anions* or *anion coordination chemistry* has been until now one of the aspects least explored. At first glance this seems a little bit surprising in view of the fundamental role anionic species play in many mineral or biological processes.

Therefore, at this stage it seemed necessary to organize a book with the aim of presenting the actual state of the art in this field, as well as the possible future developments and perspectives. To do this we have asked for the participation of different scientists in order to provide a wide panorama of the different aspects of anion coordination chemistry. The first chapter deals with presupramolecular anion chemistry, or how some of these ideas now attributed to the supramolecular era were extensively used in the past in phase-exchange or phase-transfer processes. The second chapter presents a historical point of view in which, starting from the finding of halide inclusion in 1967 by bicyclic diammonium receptors (katapinands), the most outstanding events that have marked this chemistry are presented. In the following two chapters are presented the most familiar types of natural and artificial molecules that can act as anion receptors. The concepts of preorganization and chemical design are introduced and discussed. The next chapters are devoted to structural, thermodynamic, electrochemical, and photochemical aspects of anion coordination. Owing to the importance of computer methods for the design of receptors and for the understanding of many host-guest relations, a chapter discussing this subject has been included. Finally, the last two chapters are devoted to catalytic aspects and to the perspectives and applications this chemistry is finding in many different fields.

Although some of the chapters on special themes have review characteristics, a comprehensive style has always been pursued. Therefore, we would be satisfied if this book could be of help both to researchers working in this or related fields and also to advanced science and particularly chemistry students.

We would like to thank very warmly all the chapter authors who have readily understood the importance of producing a book having the desired characteristics, and who have contributed exceptionally well-written works in all senses. We are also very grateful to Professor Jean-Marie Lehn for his eloquently written Foreword.

And last but not least, we would also like to acknowledge the patience of our families and co-workers, who, without directly participating in the book, have surely suffered from the time and travels devoted to achieving this goal.

Valencia, November 28, 1996

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Physical Factors in Anion Separations

BRUCE A. MOYER and PETER V. BONNESEN

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1.1 INTRODUCTION

As dealt with at length in this volume, the topic of anion recognition encompasses an increasing body of knowledge within the area of chemical recognition. Whereas the focus of attention has recently been directed toward the synthesis and properties of receptors having preorganized Lewis acid functionalities for selective anion binding, it seemed appropriate to us to provide a brief introduction to those physical factors that have traditionally provided the basis for anion separations. It is certainly true that attaining good separations of

anions does not necessarily require a host-guest approach. In our zeal to explore novel anion receptors, it has been perhaps easy to overlook the progress that has been made with simple monofunctional solvent-extraction reagents familiar to analytical chemistry,¹⁻⁴ hydrometallurgy,⁵⁻⁹ and the nuclear industry¹⁰ since the 1940s. The physical and chemical phenomena associated with anion separations in such systems have been well described in a number of reviews and books.¹¹⁻¹⁶ Similarly, the field of resin anion exchange has grown in maturity.^{13,17-19} While it may therefore be appreciated that highly effective anion separation processes have been devised based on traditional approaches, one may also appreciate that the means by which the underlying chemical driving forces may be manipulated to achieve a particular selectivity on demand are still rather limited. Basically, one has principles of solvation and electrostatics as tools, and these lead to anion separations based on anion properties such as size, hydrophobicity, and charge. Not surprisingly, the ordering within series of anions recurs persistently in many traditional separation systems, whether they are solvent or resin based and whether the anion-extraction equilibria involve true anion exchange or ion-pair extraction. Although limited changes in the ordering can be effected, gross reversals or peak selectivity have rarely been seen. Thus we may regard the traditional separation systems as representing a collective "baseline" by which it may be possible to judge the effectiveness and uniqueness of anion recognition by novel host molecules.

This chapter primarily describes anion-exchange separations by liquid-liquid extraction and resin systems. Parallels will be drawn with ion-pair extraction systems, which obey much the same selectivity relationships with regard to the anion transfer. Both anion-exchange and ion-pair extraction systems effect a spatial separation of anions from one phase to another, as opposed to homogeneous complexation processes studied commonly in coordination chemistry. Mass transfer of solute species across phase boundaries and a concomitant change in solute solvation characterize the majority of separation processes applicable to the liquid phase, and the solvation change strongly influences overall driving force and selectivity. The traditional anion-exchange reagents are typically ion pairs in which the cation is either restricted to a solvent phase because of the cation's hydrophobic character (solvent extraction) or immobilized on a polymer backbone (resin anion exchange). Such reagents may be viewed as "simple" in their composition, but their actual behavior has usually not turned out to be simple upon close inspection. In solvent extraction, ion pairs aggregate strongly because of their highly dipolar nature; the aggregates range from dimers to inverted micelles. Anions may include not only simple mineral acid anions but also complex anions, typically an assembly of aqueous anionic ligands coordinated to one or more metal cations. Although recent terminology was not available in the 1950s as such systems were beginning to be understood, we now can recognize such behavior as none other than "supramolecular." Certainly as we seek to develop novel supramolecular systems for separations and other uses, knowledge of the

underlying behavior of the "simple" reagents can furnish a valuable foundation for advancement.

Writing this review naturally brought about the following question: Do the traditional anion-exchange systems "recognize" the anions that are selected? If selectivity stems predominantly from electrostatic interactions, as widely thought, then it depends fundamentally on the variables of ionic radius and dielectric constant. In principle, for spherical anions of a given charge type, size is the determining factor, and as we describe at length later, extractive preference effectively increases with increasing anion size. Thus no single anion is preferred, since it is generally possible to find a more highly preferred anion. In this case, the authors would argue against the use of the term *recognition*. Rather, the system exhibits "bias" in one direction or another. *Recognition* would, by contrast, be obtained in those systems that could be designed to depart from such baseline selectivity. As discussed in later chapters in this volume, such departures must entail some three-dimensional quality of a host or ligating species, entailing matching contours or bonding sites. Some of the distinguishing features of *bias* and *recognition* in chemical systems are compared in Fig. 1.1. Traditional anion-exchange systems lie near the left side of the figure. They involve primarily physical interactions and solvation without benefit of stable coordinate bonding. However, one could maintain that some of the traditional anion-exchange systems do indeed involve departures from the simple *bias* type of selectivity, and in such cases, one can point to specific effects such as steric interactions, multiple hydrogen bonding, or unique organization of the extraction complex. Such systems arguably entail primitive aspects of *recognition*. For most such systems, however, the authors will consciously avoid the term *recognition* when only *bias* is indicated. The terms *selectivity*, *preference*, or *discrimination* will be treated as all-inclusive.

As a matter of organization, this chapter will first outline some relevant electrostatic principles. Their use and limitations in devising and understanding separation schemes will then be discussed. We will present examples of anion exchange in liquid-liquid systems, defining "baseline" bias and pointing out a few specific departures from such bias. Anion exchange in resin systems

Selectivity Type	
Bias	Recognition
Monotonic trend	Peak preference
Little geometrical preference	Geometry sensitive
Physical variables important	Bonding character important
Solvation important	Shielding from solvent
No host	Host-guest interaction
Simple ligand	Multifunctional ligand

Fig. 1.1 Factors characteristic of *bias* versus *recognition*, extreme types of selectivity.

presents unique features, since the bound functional sites lack the mobility of the liquid-liquid systems and since other physical factors come into play. Discussion of the origin of bias in resin systems together with representative examples will conclude the chapter. In view of the huge, already well-reviewed volume of literature to draw from,¹⁻¹⁹ no attempt will be made to treat the topic of anion separations comprehensively. The reader is referred to this literature for specific information that has been cataloged. Rather, from the present vantage point of chemical progress, selected systems involving simple inorganic anions will be discussed here as a means of illustrating general principles. Unfortunately, the extraction of anionic metal complexes, a topic of considerable importance for industrial applications, is beyond the present scope and will only be treated superficially as basically an extrapolation of the behavior of smaller anions.

1.2 ANION RADII, HYDRATION, AND SOLVATION

Anion charge and size come to mind as primary properties by which solvent or resin systems may distinguish different anions. Table 1.1 presents ionic radii (r) and standard molar Gibbs hydration energies (ΔG_h^0) of common inorganic anions of varying charge and size.²⁰⁻²⁹ Heat capacities,³⁰ entropies,³¹ and enthalpies^{32,33} of hydration are also available, as are other properties such as softness.³² Since the concept of anion size partially loses definition in comparing multiatomic anions, thermochemical radii^{21-24,26} derived mostly from lattice energies are also included in the table together with the familiar effective ionic crystallographic radii²⁰ where applicable. Generally, the crystallographic and thermochemical radii are mutually consistent,³⁴ notwithstanding differences that may reach as high as 0.010 nm (5%). Although most electrostatic calculations deal strictly with spherical ions, the thermochemical radii thus permit useful estimates to be made for the usual situation involving nonspherical ions. We will give preference here to the crystallographic radii in calculations, using the thermochemical radii only for multiatomic anions and implicitly assuming that anionic radii remain constant on transfer between phases. Despite the solid-state origin of the crystallographic and thermochemical radii, diffraction measurements and the results of molecular-dynamics simulations and Monte Carlo calculations have shown that the radii of ions in solution are not significantly different,³⁴ as suggested previously.²⁶ It should be borne in mind throughout this chapter that this assumption together with the treatment of multiatomic anions as spheres characterized by a thermochemical radius are only approximations. Comparisons of behavior always work best within families of chemically and geometrically similar anions.

The driving force for solvent-extraction and ion-exchange processes depends upon the state of the ion in the initial phase (here assumed aqueous) and the final phase. Since traditional reagents do not involve host molecules that completely desolvate the ion, considerable direct solvation of the ion in both

phases can be presumed. For the most elementary discussion, it is easiest to begin by considering the case where the ion is completely solvated in one phase but not at all in the other. Since the source phase is water, we will begin with the process of anion hydration.

The hydration process refers to the transfer of the bare gas-phase ion to aqueous solution:



Table 1.1 gives the values of the standard molar Gibbs energy of hydration ΔG_h° at 25°C based on the choice $\Delta G_h^\circ[H^+] = -1056 \text{ kJ/mol}$. The choice of this reference value for the hydrogen ion follows from the reasonable assumption (TATB assumption) that the solvation of tetraphenylarsonium cation and tetraphenylborate anion are identical;³⁵ the TATB assumption will be used for all single-ion thermodynamic values employed in this review. Conceptually, we may view the reverse of the hydration process, namely, the removal of the ion from water to the gas phase, to be the most elementary extraction process as well as the first step in useful thermochemical cycles representing more complicated extraction processes. Although the “extraction” of most common anions into vacuum is obviously a highly unfavorable process, one may note that this process of removing all solvation exhibits extreme bias toward large anions in closely related families such as the halides. Comparing all the anions in Table 1.1, increasing anion size generally favors transfer of the anion to the gas phase. Exceptions to the trend are obvious, however, especially with ions having acidic protons, like $H_2PO_4^-$ and $BO_2^-(H_2BO_3^-)$. Accordingly, the thermochemical radius as a single indicator somewhat imperfectly forecasts trends in anion hydration for a wide variety of inorganic anions. Notwithstanding the experimental limitations in measuring thermochemical radii and standard Gibbs hydration energies, the data thus suggest that primitive recognition factors may play a nonzero role even in a process as fundamental as hydration.

Ion solvation represents the analogous and more general process of transferring an ion from the gas phase to any pure solvent, including water:



Much theoretical effort has been devoted to developing mathematical models describing the standard Gibbs energy change ΔG_s° of this process for cations and anions of varying charge types and ionic radii.^{36–40} From the simple Born model the electrostatic part of the standard Gibbs energy in kJ/mol may be obtained readily, treating ions as hard spheres in a continuous dielectric:

$$\Delta G_{\text{Born}}^\circ (\text{kJ/mol}) = \frac{Bz^2}{r'} \left(1 - \frac{1}{\epsilon} \right) \quad (3)$$

where ϵ is the dielectric constant, z is the ionic charge, B is a temperature-independent constant equal to $-69.47 \text{ kJ nm mol}^{-1}$, and r' is the ionic radius