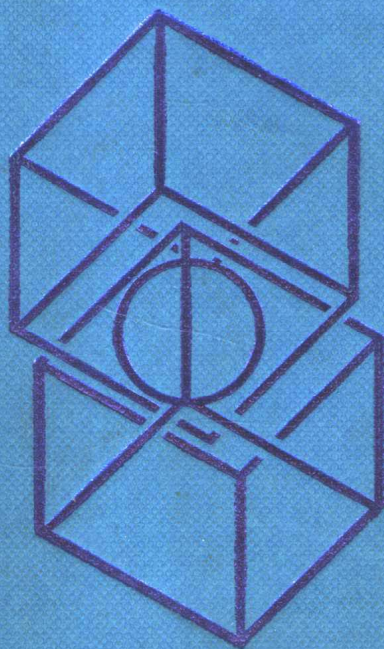

INCLUSION COMPOUNDS

VOLUME 3

Physical Properties
and Applications

Edited by
J.L. ATWOOD
J.E.D. DAVIES
D.D. MACNICOL



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Volume 3

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PREFACE

In September 1980 the Institute of Physical Chemistry of the Polish Academy of Sciences hosted the First International Symposium on 'Clathrate Compounds and Molecular Inclusion Phenomena' at Jachranka, near Warsaw. At this timely meeting, the first devoted entirely to all types of inclusion behaviour, the unanimous opinion of the participants was that every effort should be made to draw together in print the various threads from which the rich tapestry of Inclusion Chemistry is currently being woven.

As a first step in this direction, the proceedings of the conference were published in special issues of the *Journal of Molecular Structure* (Volume 75, Number 1, 1981) and the *Polish Journal of Chemistry* (Volume 56, Number 2, 1982). However, to obtain a more global modern picture of Inclusion Chemistry it was apparent that an up-to-date Comprehensive Treatise would be necessary. In view of the rapid advances being made at present, it was clear that such a work could only be produced on an acceptable timescale, and with a sufficient depth of treatment of recent work, by inviting recognized international authorities to write on their own particular fields of interest. Accordingly, this was the plan chosen for the present work.

Earlier useful books, in English, have appeared on inclusion compounds over the years, each reflecting the state of knowledge at the time of publication, three being *Clathrate Inclusion Compounds*, Reinhold, 1962, by M. Hagen; *Non-Stoichiometric Compounds*, Academic Press, 1964, edited by L. Mandelcorn; and *Clathrate Compounds*, Chemical Publishing Company, 1970 by V. M. Bhatnagar. The most comprehensive of these is undoubtedly the book edited by L. Mandelcorn (1964) and in some ways the present treatise may be regarded as complementary to that work.

The editors note, with pleasure, the greatly increasing interest in inclusion phenomena, as evidenced by recent relevant publications on *specific* aspects of Inclusion Chemistry: *Cyclodextrin Chemistry*, by M. L. Bender and M. Komiyama, Springer-Verlag, 1977; *Host-Guest Complex Chemistry I and II*, edited by F. Vögtle, Springer-Verlag, 1981; *Ionophores and their Structures*, by M. Dobler, Wiley, 1981; *Cyclodextrins and their Inclusion Complexes*, by J. Szejtli, Akadémiai Kiadó, Budapest, 1982; and *Intercalation Chemistry*, edited by M. S. Whittingham and R. J. Jacobson, Academic Press, 1982. Also a new journal devoted to inclusion compounds *The Journal of Inclusion Phenomena* has been launched by the Reidel Publishing Company.

We have great pleasure in dedicating these three volumes to Professor H. M. Powell, FRS, whose pioneering crystallographic work laid firm foundations for subsequent work in Inclusion Chemistry.

We wish to thank Professor Powell for kindly agreeing to write the important introductory chapter; and we are indebted also to all our other contributors for their help and participation in writing this book. We must also thank the staff of Academic Press for the efficient way in which the book has been produced.

The present volume is the third of a three volume series designed to provide comprehensive coverage of all aspects of inclusion compounds. Volumes 1 and 2 reviewed structural and design aspects of inclusion compounds whilst the present volume is mainly concerned with their physical properties, applications, and biological significance.

March 1984

J. L. Atwood
J. E. D. Davies
D. D. MacNicol

Dedicated to
H. M. Powell, FRS
who laid the firm foundation on
which this book is based

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1 • THERMODYNAMIC STUDIES OF CLATHRATES AND INCLUSION COMPOUNDS

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1. General introduction

In embarking on the study of the thermodynamic properties of inclusion compounds the initial assumption which is made is that the host-lattice behaves as if it were inert. This leads to the conclusion that each thermodynamic property may be split into contributions from the host and guest substances. This assumption, which is almost universally made, has been questioned by Hazony and Ruby,¹ who have pointed out that for a β -quinol clathrate with all of the cages occupied by krypton atoms the mass of guest substance is far from negligible compared with that of the quinol associated with it, so that coupling of the motions of the components would be expected. However, a stronger case for the importance of host-guest coupling would arise if the frequency of the rattling mode of the guest molecules was close to that of important modes of the host lattice, and this generally does not