

Book Reviews

Joanna Sadlej: *Semi-Empirical Methods of Quantum Chemistry*, Ellis Horwood, Chichester, 1985, £42.50, 386 pp., ISBN 0-853121672.

This book is a translation of a Polish book published in 1977, which has been updated slightly for the English version, so that references up to the end of 1978 are included and some mention of the MNDO method is made.

The author attempts to present to a non-theoretician the various semi-empirical methods available (CNDO, INDO, NDDO and variants) and to show their applicability: of the various methods included PCILO is treated least satisfactorily, but the other methods, including RCNDO for Rydberg states, are fully described. The book therefore contains a useful summary of the various parametrisations extant.

As far as the applications are concerned it is unfortunate that the translation is relative to a point seven years ago; some of the examples chosen are no longer indicative of the usefulness of semi-empirical methods, but show rather their fallibility. In several places there are sins of omission. For instance, in the chapter on Hydrogen Bonding the author describes the CNDO/2 method as being generally excellent for the treatment of H-bonded dimers, and yet Thiel in 1978 (not referenced) showed the dangers of using that method in the water dimer system. Similarly Rein, and separately Dewar (also in 1978, also unreferenced) commented that MINDO/3 was unsuitable for H-bonding studies or for calculations on molecular complexes. No mention is made of this deficiency, which is an important one.

The ten chapters are as follows: From HMO to CNDO: The SCF method and the MO approximation; Semi-Empirical SCF LCAO Methods in the All-Valence-Electron Approximation; Semi-Empirical Form of Approximate HFR Schemes; Calculation of Molecular Properties; Conformational Analysis; Chemical Reactivity; Mechanisms and Models of Chemical Reactions; The Interpretation of Molecular Spectra; Electronic Structure and Properties of Hydrogen-Bonded Systems; Ion Hydration; Electronic Structure of Biologically Active Compounds.

In conclusion, the author does indeed achieve a useful general overview of the field as it existed in 1979, but makes perhaps too persuasive a case for the use of semi-empirical methods considering the present day potential of ab initio systems such as GAMESS or GAUSSIAN 80/82. Of course semi-empirical methods are here to stay, but the systems for legitimate study by a particular method need to be chosen with care. Which is also why this book is still valuable.

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F. Vögtle and E. Weber (eds.): *Topics in Current Chemistry, Vol. 121, Host-Guest Complex Chemistry III*, Springer-Verlag, Berlin, Heidelberg, New York and Tokyo, 1984, xiv + 224 pp. \$36.60, ISBN 3-540-12821-2.

At the end of the second decade of crown ether chemistry, many design features and applications merely hinted at in the papers and patents of the late '60s and early '70s are routine – among them the separation of metal ions by solvent extraction with crowns, chromogenic groups for analytical purposes, pendant ligating groups, and macroheterocycles attached to polymers. Separate chapters are devoted to the considerable literature which exists on these topics. The last chapter deals with current synthetic ventures on natural macrocycles, the porphyrins.

About 60% of the references in the first three chapters are to Japanese work, enabling a comprehensive overview of the substantial Japanese contribution to the development of crown chemistry. Y. Takeda (Chiba University) describes the factors affecting solvent extraction of cations with crowns, and some applications in separation and analysis. The second chapter (by M. Takagi and K. Ueno, Kyushu University) describes chromogenic crown compounds capable of selective colour reactions with alkali and alkaline earth cations. The principles of design of such reagents are discussed and many examples of their use, with details of their analytical range are given. S. Shinka and O. Manabe (Nagasaki University) focus on photofunctional crown ethers and cryptands, an idea originating in their laboratory. Photoresponsive groups are classified as components for crown ethers and a number of synthetic routes to incorporate them are outlined. The examples quoted of light-driven transport indicate the improvements in selectivity in prospect using this additional design component. Editorial laxity has, however, permitted coverage of these photofunctional materials to appear not only as the main topic in this chapter, but also in three of the other chapters, on pp. 22–25, 51–52, 58–59, and 112–113. Polymeric crowns are the topic of the fourth review. This chapter by J. Smid and R. Sinta (SUNY at Syracuse) is twice as long as the second chapter, and has five times as many references, an indication of the much greater area of literature covered. The authors have chosen to contrast the behaviour of macroheterocycles on polymer supports and as monomers, and they have selected much material of industrial applicability.

A change of emphasis from Host Guest Chemistry I and II to aza-macrocycles comes in the last two chapters. The fifth review, by T. A. Kaden (University of Basle) deals with synthesis and metal complexation of aza-macrocycles with pendant ligating groups. Synthetic procedures reviewed include selective substitution of different nitrogens. The final chapter (by J. E. Baldwin and P. Perlmutter, Oxford University) is strikingly different from the earlier ones. Improving on Nature's range of porphyrin ligands is the subject. The structure and biological function of metalloproteins haemoglobin, cytochrome P450 and cytochrome-*c*-oxidase are briefly outlined, followed by a survey of synthetic efforts to develop bridged, strapped and capped porphyrins, intended as mimics of the natural macrocycles.

The book will be a useful addition to the libraries of institutions where macrocycle research is conducted. It is well produced but unfortunately too expensive for British chemists to afford a personal copy.

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J. L. Atwood, J. E. D. Davies, and D. D. MacNicol (eds.): *Inclusion Compounds, Volume 1, Structural Aspects of Inclusion Compounds Formed by Inorganic and Organometallic Host Lattices*, Academic Press, London, 1984, \$70.

The remarkable developments in the field of inclusion compounds is certainly a result of their fascinating and unique characteristics whose study covers fundamental aspects such as the synthesis of new hosts, structural determinations, the mechanism of the inclusion process, the host-guest interactions, the reactivity of the guest molecule and the already realized – or possible – applications in the analytical, biochemical and industrial fields. In the foreword, the Editors recall how the idea of realizing an up to-date treatise on inclusion compounds was born in 1980 on the occasion of the First International Symposium on 'Clathrate Compounds and Molecular Inclusion Phenomena'. It was felt that interest in inclusion compounds spread over several fields involving researchers in numerous disciplines and, although there were important books on specific aspects of inclusion chemistry, there was a need to publish a comprehensive treatise summarizing the present state of knowledge. To reach this goal, the Editors have made a suitable selection of subjects and authors, chosen from among the most authoritative personalities in the field. This policy has proved successful.

This first volume creates a very good impression. The whole treatise has been dedicated to Professor H. M. Powell, the recognized 'Father' of inclusion chemistry, who accepted the task of writing a stimulating introductory chapter. In a well-balanced combination of theory and history, the genesis of structural chemistry and its development to embrace the inclusion concept and the spread of inclusion chemistry are presented in brilliant and elegant prose. The present state of the art and possible future developments in the design of new hosts with more than one type of enclosure and of new ways of using already known structures to obtain multicomponent inclusion compounds are offered for the reader's consideration.

The second chapter, due to T. Iwamoto, is the first dealing specifically with inorganic and organometallic host lattices. The discovery, preparation, chemical and structural features of Hofmann-type inclusion compounds of general formula $M(NH_3)_2 M'(CN)_4 \cdot 2G$ and the interesting modifications induced in the original host lattices by replacing the ammonia molecules with amines and/or the planar $M'(CN)_4$ unit with tetrahedral units are all described in a plain and accessible way.

The inclusion compounds formed by Werner MX_2A_4 coordination complexes are the object of the contribution by J. Lipkowski. Numerous clear and well drawn figures aid the presentation of the molecular structure of the MX_2A_4 complexes ($Ni(NCS)_2(4\text{-methylpyridine})_4$ being used as the main example), their molecular packing (showing the shape and size of void spaces), and the position of the guest molecule. The thermodynamic and kinetic aspect of the inclusion and desorption processes are discussed with a wealth of experimental data to give, where possible, correlations with the observed selectivity in, for example chromatographic applications.

The subsequent contribution (J. Hanotier and P. de Radzitzky) also deals with a special class of Werner complexes, diisothiocyanato tetrakis (α -arylalkylamine) nickel(II), that have been studied, in the authors' laboratory, especially for their high selectivity towards *ortho*-isomers of aromatic hydrocarbons. The reader can find details of the preparation of the inclusion compounds with a variety of aromatic isomers and the analytical data which give an indication of the selectivity of the host lattices, together with a discussion of the driving forces that affect the inclusion processes. Much of the topic is based on unpublished results but the latest references date to 1969. With the two subsequent contributions the reader enters the fascinating world of structures built up by the concatenation of polyhedra.

Chapter 5, due to G. A. Jeffrey, deals with the hydrate inclusion compounds. Historical notes, preparation and structures of 'gas' hydrates, of the per alkyl-onium salt hydrates and of the alkylamine hydrates are presented with the aid of excellent illustrations and numerous tables containing crystal data. In an appendix, Jeffrey teaches the way to construct cardboard models of the more common polyhedra in a pleasing fashion.

The zeolites, which can be described in terms of the polyhedral cavities found in them, are treated in Chapter 6. Professor Barrer, with his habitual rigour, after an appropriate comparison between clathration and zeolitic sorption, describes the structural, thermodynamic and kinetic aspects of zeolite – inclusion complexes containing metals, salts and molecules as guests. Within the limited space available (55 pp.), Barrer gives a significant and complete-enough account of the guest-zeolite complexes.

The contribution of R. Schöllhorn on intercalation compounds, the most extensive one of the book (85 pp.), stems from the analysis of a great number of experimental results and of a large variety of hosts (533 references). The subdivision of the host lattices into insulators (sheet silicates, alkali oxometallates, etc.) and those showing electronic conductivity (graphite, transition metal dichalcogenides, etc.), with a large prevalence of the latter type of hosts, enables this vast topic to be treated in an organised way. The definition of intercalation compounds as inclusion compounds obtained via a topotactic solid state process allows the author to discuss not only the layered host lattices, usually associated with the term intercalation, but also the framework host lattices (e.g. pyrochlore, β -aluminas, molybdenum cluster chalcogenides), chain-type hosts (transition metal trichalcogenides) and some molecular solids. Of great interest and relevance are the parts dealing with the ionic transport (protonic in particular) properties of intercalation compounds, related to their electrochemical applications.

The last two contributions may be regarded as accounts of the research of the authors into cyclophosphazene inclusion adducts (H. R. Allock) and liquid clathrates (J. L. Atwood). The reviewer finds the historical notes, preparation, structural considerations and inclusion behaviour of these unusual hosts which constitute an exciting and promising field of research.

The book (405 pp., supplied with very useful indexes for the subjects and authors cited) is well produced in an elegant binding and there are almost no printing errors. It will be welcome not only by researchers directly involved in host-guest chemistry, but also by solid state chemists, physicists and crystallographers.

UMBERTO COSTANTINO

J. L. Atwood, J. E. D. Davies, and D. D. MacNicol (eds.), *Inclusion Compounds, Volume 2, Structural Aspects of Inclusion Compounds Formed by Organic Host Lattices*, Academic Press, London, 1984, \$72.

Over the last two decades chemical inclusion phenomena have been the subject of considerable interest in research and application. This will continue since the prospects associated with this area of chemistry are fascinating. Numerous reviews and monographs which have been published over the years illustrate this topic from different approaches. The present volume, however, is in no regard an impression of former papers which tendentiously concentrate on the inclusion behaviour of crown compounds to (metal) ions. The editors have noted the strongly increasing interest in clathrate-type (crystal lattice) and molecular inclusion phenomena and focus on this selected topic (with some few exceptions). Earlier monographs

having a similar object, are older than ten years. They need to be up-dated. Does the present work meet this requirement?

The book covers eleven chapters of fairly different lengths.

Chapter 1 (45 pages, by D. D. MacNicol) is concerned with structural and design aspects of the inclusion compounds of hydroquinone, phenol, Dianin's compound and related systems. Although classical host-types are touched, this contribution (fortunately) is not related to historical ballast, but considers well presented recent synthetic and structural work of the author and others.

Similar facts hold for *Chapter 2* (20 pages, by K. Takemoto and N. Sonoda) which reflects the state of knowledge on the inclusion compounds of urea, thiourea and selenourea.

Of less novelty (most of the cited literature dates from the sixties) is the contents of *Chapter 3* (Inclusion Compounds of Perhydrotriphenylene, 26 pages, by M. Farina).

Chapter 4 (24 pages, by A. Collet) deals with the inclusion chemistry of cyclotrimeratrylene and of related hosts. To my knowledge this contribution represents the first extensive review on that sector.

In *Chapter 5* (45 pages, by D. D. MacNicol) the significance of a group of molecules called 'hexa-hosts' is emphasized. Researchers, who are familiar with modern inclusion chemistry will be aware of the intelligent strategy behind this molecular structure from many review papers, but this chapter, indeed, gives the most comprehensive survey of the whole field. Hosts having trigonal symmetry are also touched.

The synthesis, the geometrical properties, and the inclusion behaviour of trianthranilides, which are the nitrogen analogues (amides) of trisalicylides (e.g., tri-*o*-thymotide), are subjects of *Chapter 6* (36 pages, by W. D. Ollis and J. F. Stoddart). Conformational problems are discussed in detail.

Chapter 7 (22 pages, by E. Giglio) refers to the inclusion chemistry of deoxycholic acid, also a classical host system. This work, however, is interspersed with recent structural results.

The outstanding behaviour of cyclodextrins and of their inclusion compounds have been the motive for many authors to publish comprehensive papers (e.g. the books edited by Bender, and by Szejtli). The present contribution in *Chapter 8* (28 pages, by W. Saenger) concentrates only on structural aspects of modern cyclodextrin chemistry.

Chapter 9 (74 pages, by I. Goldberg) is entitled 'Complexes of Crown Ethers with Molecular Guests'. Cyclic crowns, coronands, and spherands, as well as open-chain podands, commonly known as (metal) ion sepulchres, are shown in their behaviour to complex various ammonium and uncharged molecular guests. Contrasting the limitation in subject, a full section is also devoted to the metal ion complexes of noncyclic podands; the same is true for some of the complexes of spherands. The whole discussion in this chapter is based on a structural point of view.

Chapter 10 (68 pages, by B. Dietrich) provides the readers with an impressive survey of the chemistry of cryptands (oligocyclic crown analogues), including host synthesis, cation and anion complexation, and a brief account of the most important application aspects. An immense collection of references (345 quotations) is a further special merit of this contribution.

Chapter 11 (46 pages, by J. E. D. Davies, P. Finocchiaro, and F. H. Herbstein) is rather unbalanced in its scientific content. Some of the host molecules, e.g. trimesic acid, are subject of a whole section, others, although no less important, are condemned to take up a modest position in a tedious listing of compounds. In addition, the section dealing with inorganic and organometallic host lattices does not match quite well the original intention of the book, which, according to the subtitle, is 'Structural Aspects of Inclusion Compounds Formed by Organic Host Lattices', but would ideally fit in Volume 1 of the three volume series.

Apart from the small criticism stated on some points, the book is of good quality. It is well produced with relatively few printing errors. There are extensive tables of data accompanied by a number of well organized illustrations and a reasonably complete collection of literature which reaches up to 1982 for most of the contributions. The editors are also to be commended on including an extensive author and subject index.

This book, really, is recommended strongly to all those interested in the fascinating area of inclusion chemistry. Without doubt, accompanied with Volumes 1 and 3 of the series, the work represents the most complete and up to date review on inclusion phenomena that is presently available. It is to be hoped that the relatively high price of the book will not keep interested persons from buying it.

Reconsidering the question at the beginning, this book is complete up to the date of approximately 1982. Because of the rapid development of the field, a further monograph should be desirable in the near future.

EDWIN WEBER

J. L. Atwood, J. E. D. Davies, and D. D. MacNicol (eds.), *Inclusion Compounds, Volume 3, Physical Properties and Applications*, Academic Press, London, 1984, \$98.

This third volume in the series on inclusion compounds features 16 chapters devoted to the physico-chemical properties of inclusion compounds, to their use in practical processes and to the study of enzyme models and of transport processes based on complexing agents.

This book brings together topics which are usually either not available in review form or scattered through the literature. The sections on physical methods (IR, Raman, ESR, Mössbauer, photoelectron, NMR and NQR spectroscopic studies) and physicochemical properties (thermodynamic and structural features) provide thorough overviews which cover solid state inclusion compounds (clathrates, zeolites) as well as molecular inclusion complexes.

The chapters on applications will be very useful since it not only provides a detailed picture of what has been realized, but also gives access to numerous data and results only available in patents; this is especially true for the industrial applications of cyclodextrins in various areas from separation procedures to the food industry.

Finally a series of chapters describe the binding properties of cyclodextrins and of synthetic macrocyclic receptors (crowns, cryptands) and the development of enzyme models and of transport processes based on these features. They provide a timely and authoritative discussion of these areas which are subject to very active current research.

In conclusion, this volume will be of interest and of use to all those concerned with fundamental studies as well as with industrial applications of inclusion complexes. Attractive though its features are, its price will probably limit its availability to libraries and to laboratories.

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