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Inclusion Compounds

Volume 1

Structural Aspects of Inclusion Compounds
Formed by Inorganic and
Organometallic Host Lattices

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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, Akademiai Kiado, 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 first of a three volume series designed to provide comprehensive coverage of all aspects of inclusion compounds. Volume 1 is principally concerned with structural and design aspects of inclusion compounds formed by inorganic and organometallic host lattices. Volume 2 is concerned with similar aspects of inclusion compounds formed by organic host lattices, whilst Volume 3 will concentrate on the physical properties and applications of inclusion compounds.

December 1983

J. L. Atwood

J. E. D. Davies

D. D. MacNicol

Contents

List of contributors	v
Preface	vii
Contents of Volumes 2 and 3	xiii

Chapter 1. Introduction *H. M. Powell*

1. Inclusion	1
2. Genesis, fall and rise of structural chemistry	2
3. The measurement of structures	9
4. Crystal chemistry embraces inclusion compounds	11
5. The spread of inclusion chemistry	12
6. Scope of these volumes	13
7. Present and prospective elaboration of inclusion structures	15

Chapter 2. The Hofmann-type and related inclusion compounds

T. Iwamoto

1. Historical	29
1.1. The discovery of Hofmann's clathrate	29
1.2. The Hofmann-type inclusion compounds	31
2. Hofmann-type inclusion compounds	32
2.1. Structural features	32
2.2. Chemical features	37
2.3. Metal complexes related to Hofmann-type hosts	40
3. Modification of Hofmann-type inclusion compounds	42
3.1. Strategy of modification	42
3.2. Bridging of ambidentate ligand between cyanide sheets	44
3.3. Host structures with a tetrahedral moiety	47
3.4. Hosts with bulky amine ligands	52

Chapter 3. Inclusion compounds formed by Werner MX_2A_4 coordination complexes *J. Lipkowski*

1. Introduction	59
2. Structure of the inclusion compounds formed by MX_2A_4 coordination complexes	60
2.1. Molecular structure of the host MX_2A_4 complexes	60
2.2. Molecular packing in the known host crystalline lattices	64
2.3. Effects of absorption of the guest components on the molecular and crystal structure of the host	71
3. Composition of the inclusion compounds formed by the MX_2A_4 hosts	75
3.1. Saturation capacities	75
3.2. Inclusion isotherms in the systems: gaseous guest-solid host	77

3.3. Sorption equilibria in the systems: solid inclusion compound—liquid solution of guests	79
4. The role of steric effects in intramolecular (host) and intermolecular (guest—host) interactions in Werner type inclusion compounds	85
4.1. Energy of intramolecular interactions within the host molecules	85
4.2. Analysis of thermochemical data on enthalpy of inclusion	88
4.3. Some interrelations: structure—selectivity of inclusion	92
5. Kinetics of the sorption—desorption processes	92
5.1. Desorption of the guest (G) from $\beta\text{-Ni(NCS)}_2(4\text{-MePy})_4\cdot\text{G}$ to a gas phase	92
5.2. Analysis of chromatographic data on the rate of the mass exchange processes in the systems: "clathrate" sorbent—liquid mobile phase	95
5.3. Kinetic course of the reaction: $\alpha\text{-Ni(NCS)}_2(4\text{-MePy})_4 + \text{G}_{\text{liq}} \rightarrow \beta\text{-Ni(NCS)}_2(4\text{-MePy})_4\cdot\text{G}$	97
5.4. Thermogravimetric studies	99
6. Concluding remarks	100

Chapter 4. Inclusion compounds of diisothiocyanatotetrakis(α -arylalkylamine) nickel(II) complexes *J. Hanotier and P. de Radzitzky*

1. Scope	105
2. Historical background	106
3. Preparation of the inclusion compounds and inclusion results	107
3.1. Explanation of the tables	108
4. Driving forces in inclusion compound formation	111
4.1. Electronic interactions	111
4.2. Steric factors	115
5. Influence of the optical isomerism of α -arylalkylamines	119
5.1. Inclusion compound formation by the complexes of optically pure amines	119
5.2. Inclusion compound formation from two-base complexes	121
5.3. Exchanges between coordinated and free amine	125
6. Structural study	128
7. Applications	132

Chapter 5. Hydrate inclusion compounds *G. A. Jeffrey*

1. Introduction	135
2. History	136
3. The structural basis for the formation of hydrate inclusion compounds	141
4. The clathrate hydrate structures	150
5. The per alkyl-onium salt hydrate structures	159
6. The position of the anions	164
7. The alkylamine hydrate structures	169
8. Miscellaneous hydrate inclusion structures	178
9. Conclusion	182
Appendix	185

Chapter 6. Zeolite inclusion complexes *R. M. Barrer*

1. Zeolites	191
2. Intrazeolitic channels and cavities	192
3. Distributions of guest molecules	199
4. Zeolitic sorption and clathration: a comparison	203
5. Metal-zeolite complexes	206
6. Salt-zeolite complexes	210
7. Molecule-zeolite complexes	213
7.1. Isotherm contours	213
7.2. Thermodynamic aspects of equilibria	217
7.3. Differential heats and energies	225
7.4. Entropy, heat capacity and isotherm models	232
7.5. Non-uniform sorbents	237
8. Diffusion and molecular dimensions	241
9. Concluding remarks	245

Chapter 7. Intercalation compounds *R. Schöllhorn*

1. Introduction	249
2. Formation, structure, bonding and reactivity: basic aspects	250
2.1. Insulator hosts	253
2.2. Host lattices with electronic conductivity	255
2.3. Limits of validity of the model schemes	257
3. Insulator host lattices	259
3.1. Framework host lattices	259
3.2. Layered materials	265
3.3. Chain structures	271
4. Host lattices with electronic conductivity	271
4.1. Framework structures	271
4.2. Layered structures	284
4.3. Chain type host units	301
4.4. Hydrogen bronzes	303
4.5. Molecular solids	311
5. The charge transfer problem	316
5.1. Metal intercalation compounds	317
5.2. Molecular intercalates	322
6. Ionic transport and molecular dynamics	325
6.1. Metal ions in host lattices	325
6.2. Proton transport	327
6.3. Molecular guest species	328
7. Physical properties	330
8. Applications	331
9. Conclusions	334

Chapter 8. Cyclophosphazene inclusion compounds *H. R. Allcock*

1. Background and scope	351
2. Inclusion behaviour of compounds 3-7	354
3. Selective absorption and separation of guest molecules	356
4. Crystal and molecular structure	358

5. Inclusion and polymerization of unsaturated organic guest molecules	365
6. Molecular motion of guest molecules	368
Chapter 9. Liquid clathrates J. L. Atwood	
1. Introduction	375
1.1. Definition of liquid clathrate behaviour	375
1.2. Historical development	376
2. Synthesis and structure of parent compounds, $M[Al_2R_6X]$	377
2.1. Synthesis	377
2.2. Structure	379
3. Preparation and composition of liquid clathrates	386
4. Origin of liquid clathrate behaviour	393
5. Liquid clathrates from parent compounds which do not contain aluminium alkyls	399
6. Applications	402
6.1. Separations	402
6.2. Coal liquefaction	403
Author index	407
Subject index	417

Contents of Volume 2

Structural aspects of inclusion compounds formed by organic host lattices

Chapter 1. Structure and design of inclusion compounds: The clathrates of hydroquinone, phenol, Dianin's compound and related systems <i>D. D. MacNicol</i>
Chapter 2. Inclusion compounds of urea, thiourea and selenourea <i>K. Takemoto and N. Sonoda</i>
Chapter 3. Inclusion compounds of perhydrotriphenylene <i>M. Farina</i>
Chapter 4. Inclusion compounds of cyclotrimeratrylene and related host lattices <i>A. Collet</i>
Chapter 5. Structure and design of inclusion compounds: The hexa-hosts and symmetry considerations <i>D. D. MacNicol</i>
Chapter 6. The trianthranilides: A new class of organic hosts <i>W. D. Ollis and J. F. Stoddart</i>
Chapter 7. Inclusion compounds of choleic acids <i>E. Giglio</i>
Chapter 8. Structural aspects of cyclodextrins and their inclusion complexes <i>W. Saenger</i>
Chapter 9. Complexes of crown ethers with molecular guests <i>I. Goldberg</i>
Chapter 10. Cryptate complexes <i>B. Dietrich</i>
Chapter 11. Inclusion compounds formed by other host lattices <i>J. E. D. Davies, P. Finocchiaro and F. H. Herbstein</i>

Contents of Volume 3

Physical properties and applications

- Chapter 1.** Thermodynamic studies of clathrates and inclusion compounds
N. G. Parsonage and L. A. K. Staveley
- Chapter 2.** Spectroscopic studies of inclusion compounds *J. E. D. Davies*
- Chapter 3.** NMR, NQR and dielectric properties of clathrates *D. W. Davidson and J. A. Ripmeester*
- Chapter 4.** Crystallographic studies of inclusion compounds *G. D. Andreotti*
- Chapter 5.** Host lattice-guest molecule energy transfer processes *A. Guarino*
- Chapter 6.** Applications of inclusion compounds in chromatography *D. Sybilska and E. Smolkova-Keulemansova*
- Chapter 7.** The sorptive abilities of tetracyano complexes *A. Sopková and M. Singliar*
- Chapter 8.** Isotopic fractionation using inclusion compounds *N. O. Smith*
- Chapter 9.** Enantiomeric selectivity of host lattices *R. Arad-Yellin, B. S. Green, M. Knossow and G. Tsoucaris*
- Chapter 10.** Inclusion-polymerization *M. Farina*
- Chapter 11.** Industrial applications of cyclodextrins *J. Szejtli*
- Chapter 12.** Cycloamylose-substrate binding *R. J. Bergeron*
- Chapter 13.** Reactions of inclusion complexes formed by cyclodextrins and their derivatives *I. Tabushi*
- Chapter 14.** Enzyme models related to inclusion compounds *R. Breslow*
- Chapter 15.** Enzyme-substrate interactions *L. N. Johnson*
- Chapter 16.** Cation transport in liquid membranes mediated by macrocyclic crown ether and cryptand compounds *D. W. McBride, R. M. Izatt, J. D. Lamb, and J. J. Christensen*

1 • INTRODUCTION

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1.	Inclusion	1
2.	Genesis, fall and rise of structural chemistry	2
3.	The measurement of structures	9
4.	Crystal chemistry embraces inclusion compounds	11
5.	The spread of inclusion chemistry	12
6.	Scope of these volumes	13
7.	Present and prospective elaboration of inclusion structures	15

1. Inclusion

Inclusion Chemistry has developed since the two words, or related pairs, came into conjoint use. There was a confluence of two streams of thought, one derived from a simple and very old observation that some natural objects, by reason of their shape and construction, may act as containers of other things. This perception is inherent in any recognition of any kind of shell as a shell, and in any deliberate separation of its content. The survival efforts of birds, bees, tree-rats and their relatives imply that it appeared on Earth long before man.

So from the beginning man was conscious of shell, peel and skin. Also he had a highly developed hand directly usable as an enclosing device and basic to much achievement since then. Successor man has used this hand to make enclosures for himself and his family, for his animals and other possessions, for his friends, fellow citizens, slaves and prisoners of varying degrees, and for his own remains. In some form some of these things are today repeated for the individual who is so familiar with the idea that he

uses it in myth and metaphor, claiming, sometimes, to be cribbed, cabined and confined, bound in (but by his own fears) or, maybe, seeing himself, or another, as a prisoner (but of system, doctrine, conscience and the like). In one way or another everybody understands what it is to be hemmed in.

2. Genesis, fall and rise of structural chemistry

The second stream of thought, the theory of chemistry, is not so simple. Some of the transmutations of matter that are called *Chemistry* are plain to see. Those that go with life are continuous and the influence on them of heat, light and water would be noticed long ago, but the nature and process of change is unseen. To the early highly developed mind many observed chemical changes did not necessarily suggest transmutation but may have appeared as creation in apparent growth from nothing, or as annihilation in decay or fire. So for a time, measurable in the millions of years, when humans had clear and practical ideas about inclusion they had no understanding of chemistry. Empirical knowledge of the subject accumulated over a long period. Experiment may be dated at least since the controlled use of fire but it is barely two centuries since the formulation of a reasonably coherent atomic theory with immutable elements and identifying relative weights of their atoms. The theory was based on recognition and weighing of all participants in a chemical change. Although most of its postulates have been abandoned in the present century its "laws" were accurate enough to direct an enormous growth in chemistry. Intricate arguments, involving physical and chemical observations as well as the combining weights, led chemists to put forward the reasoned *formula* as a representation of chemical make-up that provided the key to reactivity and synthesis.

Inevitably these consistent formulae, which gave the numbers of the various atoms somehow joined to form a compound, led to thoughts about the arrangement of the atoms. Multiplicity of isomers and their relationships to parent substances could be explained if the atoms in a molecule were in some order which could be varied for different isomers of the same overall composition. It then became necessary to account for the existence of isomers which had the same atoms in the same sequence. In the extreme case two isomers were indistinguishable except in effects which could be related to a special symmetry condition, the non-identity of a structure with its mirror image. Optical activity was already known in quartz crystals and had been correlated with the two enantiomorphous crystal forms. The chemical structural formula had to be extended into three dimensions. That molecules had characteristic shapes seemed to be proved and the hypothesis

of the "tetrahedral" carbon atom and similar ideas developed as guides to speculation on these shapes.

In the earliest stages of these developments, chemical structures, even atoms, were by some accepted as little more than convenient philosophic aids. The arguments for them were complex, involving a number of simultaneous postulates, not easily susceptible to independent testing, and always the conclusions offered were in terms of eternally invisibles. Chemical formulae were things on paper and, at that time, the suggestion that one of them might represent something that could act as a fence might have attracted derisory comparison with the gates of the upper and the nether regions.

Soon, however, after Pasteur's triumphs, when van t'Hoff set down the principles of chemistry in space there was the compelling evidence of continual and increasing success of synthetic chemistry based on structural formulae. Derision, attempted in this case, failed in its purpose. The need grew for models showing the scaled-up molecule. Confidence in these representations grew and chemistry was discussed in terms of their structural and even mechanical characteristics. Inspired by the behaviour of variously constructed models, speculation arose about the forms, rigidities and even the "strains" of ring systems. Though the molecules remained invisible and of unknown absolute dimensions they were conceived as structures not unlike those so long familiar on the larger scale of ordinary life. Although the absolute dimensions of molecules and their component atomic groups were unknown there were sound ways of inferring some relative values. Avogadro's hypothesis concerning gases led directly or otherwise to molecular weight and hence the molecular volume of a compound in the condensed state. Measured molecular volumes in related compounds showed sufficient additivity for the reasonable deduction that each $-\text{CH}_2-$ group in a chain occupies much the same space as any other, and the argument can be adapted to more complex structures. The whole success of structural organic chemistry, including the complexities of ring structures, depended (though not exclusively) on the representation in structural formulae of similar interatomic links by similar lengths.

The concept of molecular structure was strengthened through independent lines of thought. The invisible was not unknowable. Extensions of the broadly convincing simple kinetic theory of gases showed molecules as something more than small spheres of mass m and velocity v . Specific heats of gases were measured in numbers which distinguished monatomic, diatomic and other simple molecules as surely as if the atoms were being counted directly. More complex molecules were noticed in the same way though the counting was not so certain. The effects arise from the ways in which polyatomic molecules can rotate and their component

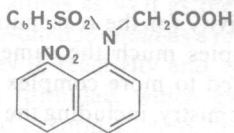
parts undergo relative motion. Molecular spectra confirm and amplify this knowledge.

Both the internal movements of a molecule and its interactions with other approaching molecules are closely related to the notion of enclosure which has the implication that something impedes the free movement of whatever is enclosed or approaches. From these movements two essentials are observed, an embryonic form of enclosing action and the rigidity necessary in potential cage-forming material.

A molecule such as tetraethylmethane, with some structural resemblance to an octopus, could become involved, during high-velocity collision with another, in a form of wrestling encounter denied to less flexible particles. The effect is revealed in comparisons of viscosities and thermal conductivities of suitable gases. It demonstrates restriction of free molecular movement by action which amounts to a temporary partial imprisonment of one molecule by another.

A degree of rigidity in molecules is implied by the all-important persistence of certain frameworks in substitution reactions. Classical chemical methods for determining structural formulae depend on this persistence and also reveal mechanical-like effects more directly related to rigidity. Some molecular structures undergo rearrangements, some invert easily and others require greater activation energy. The existence of unusual enantiomers shows that sometimes the so-called free rotation about the line of a single bond is blocked. The energy of activation for unblocking can be found by study of the racemization.

The *N*-benzenesulphonyl derivative of *N*-(8-nitronaphth-1-yl)glycine is resolvable because the nitro group interferes with free rotation about the



(1)

line of the bond from the glycine nitrogen to the ring. The effect is conditional on the maintenance of a framework which preserves the positions of the two nitrogen-to-ring bonds. Experimental information on heats of formation of suitable substances provides some evidence on the resistance of bonds to stretching and bending so that, even without the present extensive knowledge of force constants, it could be concluded that many molecular frameworks would be little distorted by the impact of a molecule having the average kinetic energy corresponding to room temperature. This is true

of many ring compounds such as the naphthalene parent of the compound above.

At some stage during the development of structural formulae there would have been nothing implausible in the suggestion of a structure capable of enclosure. When Wöhler¹ and Clemm² made the first quinol clathrates structural chemistry had developed insufficiently for this type of explanation. A substance passing the test for a new compound, in that it had its own characteristic properties, including crystalline form, different from those of its components, was formed by addition of a molecule of hydrogen sulphide (Wöhler) or sulphur dioxide (Clemm) to three molecules of quinol. For hydrogen sulphide a molecular ratio of 1:4 was also reported. The facts were recorded, not understood and wisely left to rest while other more comprehensible chemical matters were pursued. A period of great progress in structural chemistry was about to start based on a fuller exploitation of Avogadro's hypothesis. After van t'Hoff's clarification (1874) of chemistry in space, molecules became such well established structures that they could be imagined as forming a barrier. In 1886 Mylius,³ who like Wöhler and Clemm was trying to do something else, obtained a quinol clathrate, containing, in this case, formic acid and carbon monoxide, as he showed, and some vacant spaces of which he could not know. He analysed many samples, found a baffling lack of correlation between hydrogen and carbon content, but was able to determine carbon monoxide and formic acid content independently of elementary analysis. He concluded that there was no ordinary chemical combination between quinol and the other components. His suggestion that during crystallization the quinol molecules were somehow able to lock in the volatile material is something more than a restatement of his observations. "What else could he say?" it may be asked, and the answer may be "nothing", but he broke the silence since Wöhler and put some reason where none had been offered before. The state of chemical theory did not allow development of the vague "somehow able to lock" into a more definite proposal and the state of experiment did not include any means of directly locating atoms and so settling the question. In the interval between Mylius and a direct solution half a century was available for reflection on other ideas and phenomena relevant to inclusion.

Some thought was given to the ways in which components may be packed together in crystals. This shows that vacant spaces are possible. The closest packing of spheres of radius r leaves spaces the largest of which could contain other spheres of radius $0.414r$, and of about one fourteenth the volume of the larger spheres. For a globular molecular grouping to leave such spaces large enough to contain a second component it would need to contain something like fourteen times as many atoms as the enclosed