Inclusion Compounds

Volume 2

Structural Aspects of Inclusion Compounds formed by Organic 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 recognised 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 Reidel.

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 second 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, while Volume 3 concentrates on the physical properties and applications of inclusion systems.

January, 1983

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

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1 · STRUCTURE AND DESIGN OF INCLUSION COMPOUNDS: THE CLATHRATES OF HYDROQUINONE, PHENOL, DIANIN'S COMPOUND AND RELATED SYSTEMS

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1. Introduction

Host molecules possessing at least one phenolic hydroxyl group have played a vital role in the development of the chemistry of crystalline multimolecular inclusion compounds. Viewing this fascinating area in historical perspective one may identify as important landmarks the early *chance* discoveries of key host molecules such as hydroquinone (**1**), phenol (**2**), and Dianin's compound (**3**); the subsequent X-ray elucidation of the crystal structures of adducts of these hosts; and, comparatively recently, the successful *design* of new host molecules belonging to the phenolic class. A number of reviews have appeared,[1–26] and the principal aims of the present chapter are to

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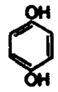
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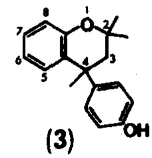
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cover recent structural work on phenolic hosts and to describe in some detail the successful synthesis of new hosts by *structural modification of a* known host, Dianin's compound (3). Other important aspects of the key phenolic class of host molecule are discussed in detail elsewhere, as indicated: infrared and Raman studies (Volume 3, Chapter 2), thermodynamic considerations (Volume 3, Chapter 1), and dielectric and magnetic resonance investigations (Volume 3, Chapter 3). In the present chapter some practical applications are mentioned, and a brief survey of less-studied phenolic hosts is also given. The successful synthesis of new host molecules with no *direct* structural relationship to any known host, based on the recognition of the importance of the (OH···O) hydrogen-bonded hexameric unit found in many phenolic host lattices, represents a significant step forward in host design, and this is considered separately in Volume 2, Chapter 5.

2. Hydroquinone

2.1. β-Hydroquinone clathrates

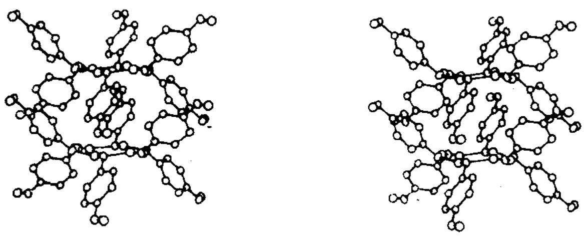
The history of adducts of hydroquinone, or quinol (1), already reviewed,[1] dates back into the nineteenth century: in 1849 Wöhler[27] found H_2S to be trapped by 1, then, ten years later, Clemm[28] found SO_2 to be similarly retained; and in 1886 Mylius,[29] discovering the inclusion of carbon monoxide by 1, made the very shrewd observation that perhaps the molecules of hydroquinone were somehow able to lock the volatile component into position without chemically combining with it. It was not until the 1940s, however, that the pioneering X-ray studies of Powell and coworkers[30,31a,32–34] firmly established the true cage, or clathrate,[35] nature of these intriguing systems. In fact, hydroquinone can exist in three crystal modifications designated α, β, and γ forms, the α-form being the stable form at room temperature. The monoclinic γ-form is produced by sublimation or by rapid evaporation of a solution of 1 in ether. The β-form is the most versatile, however, and the classical studies of Powell and colleagues[30,31a,32–35] established that three crystallographically distinguishable kinds of β-hydroquinone clathrate host lattice, now termed[36] Types I-III, can exist, all having

Table 1. Selected crystal data for β-hydroquinone clathrates and other forms of **1**

Designation	Space group	Lattice parameters[a]	Guest	Hexamer dimensions (O···O)	Ref.
β-form (Type I)	$R\bar{3}$	$a = 16.613(3)$, $c = 5.4746(5)$ Å, $Z = 9$	None	2.678 (3) Å	37
β-form (Type I)	$R\bar{3}$	$a = 16.616(3)$, $c = 5.489(1)$ Å, $Z = 9$ (host)	H_2S	2.696 (1) Å	41
β-form (Type II)	R3	$a = 16.31(5)$, $c = 5.821(1)$ Å, $Z = 9$ (host)	SO_2	2.727 (6) Å, 2.733(6) Å	31(b)
β-form (Type II)	R3	$a = 16.621(2)$, $c = 5.562(1)$ Å, $Z = 9$ (host)	MeOH	2.653(5) Å, 2.779(5) Å	45
β-form (Type II)	R3	$a = 16.650(1)$, $c = 5.453(1)$ Å, $Z = 9$ (host)	HCl	2.61 (1) Å, 2.77 (1) Å[b]	47
β-form (Type II)	R3	$a = 15.946(2)$, $c = 6.348(2)$, $Z = 9$ (host)	CH_3NC	2.779 (6) Å, 2.800 (6) Å	43
β-form (Type III)	P3	$a = 16.003(2)$, $c = 6.245(2)$, $Z = 9$ (host)	CH_3CN	2.778 Å[c] (mean)	43
α-form	$R\bar{3}$	$a = 38.46(2)$, $c = 5.650(3)$ Å, $Z = 54$	None	2.677 (3) Å	49
α-form	$R\bar{3}$	$a = 38.529$, $c = 5.66$ Å, $Z = 54$ (host)	SO_2	[d]	50
γ-form	$P2_1/c$	$a = 8.07$, $b = 5.20$, $c = 13.20$ Å, $\beta = 107°$, $Z = 4$		[e]	52

[a] For $R\bar{3}$ and R3, the values of a and c given are referred to a hexagonal unit cell ($\alpha = \beta = 90°$, $\gamma = 120°$).
[b] X-ray values.
[c] Individual values for the three independent $[OH]_6$ rings are 2.792, 2.788; 2.785, 2.782; 2.745, 2.773 Å (e.s.d. 0.006 Å in each case).
[d] Not available.
[e] No hexamers present in structure, see Fig. 6(b).

the same general formula $3\,C_6H_4(OH)_2.xG$, where G represents the encaged guest molecule and x is a site occupancy factor between zero and one. Table 1 gives representative crystal data, mainly selected from recent sources, for β-hydroquinone, as well as for the α- and γ-modifications. (The crystal structures of the α- and γ-forms are discussed below.) As indicated in Table 1, the unsolvated β-form and the corresponding H_2S clathrate correspond to the Type I situation for **1**, and in such cases cavities having $\bar{3}$ (C_{3i}) symmetry are present. Figure 1a shows a stereoview of such a centrosymmetric cage of the unsolvated form. As can be seen the top and bottom of the void are formed by hexagons of hydrogen-bonded oxygen atoms; an ordered arrangement of hydrogen atoms is apparent in the $[OH]_6$ rings and host molecules point alternately above and below the mean plane of the (nearly planar) six oxygen atoms. The hexameric units forming the ceiling and floor of a given cage, as may be seen from Fig. 1b, belong to two identical, but displaced, three-dimensional interlocking networks first defined for the "empty" form by Powell and Riesz.[38] The remarkably low packing coefficient,[39] 0.62 (or 0.59 excluding the hydrogen atoms involved in hydrogen bonding[37]) may be compared with the normal range, 0.65–0.77, for most organic molecular crystals, and demonstrates the realization of an "open" structure with unfilled cavities stabilized by an extended system of



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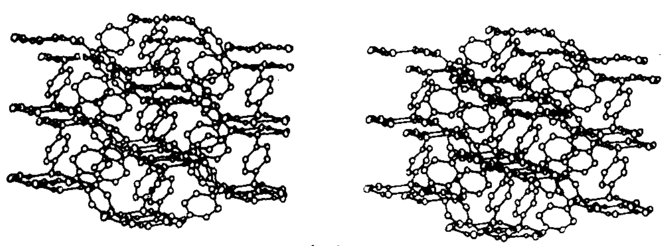

(b)

Fig. 1. Stereoviews illustrating (a) the construction of a single cage in the unsolvated form of β-hydroquinone and (b) more extended portions of the two identical, but displaced, three-dimensional networks from which cages are constructed. (Both drawn from data of ref. 37.)

hydrogen bonds. In recent X-ray work on the H_2S clathrate, undertaken to define accurately a Type I clathrate, Mak and coworkers[40,41] have found that the H_2S guest molecule, situated in an approximately spherical cavity of mean free diameter c. 4.8 Å, undergoes pronounced thermal motion, particularly in the direction of the centres of the $[OH]_6$ rings, that is, along the c-axis of the crystal. In this centrosymmetric clathrate[42] the results are consistent with rotational disorder of the guest molecule.

In Type II clathrates, such as those formed by **1** with SO_2, MeOH, HCl, or CH_3NC, a lowering of space group symmetry from $R\bar{3}$ to R3 is found, and guest accommodation is provided in cages which are still trigonal, though no longer centrosymmetric. For the relatively long guest molecule methyl isocyanide the cage length, corresponding to the c-spacing (Table 1), is markedly increased compared with the Type I systems already discussed (see below). Figure 2 illustrates the alignment of the CH_3NC along the

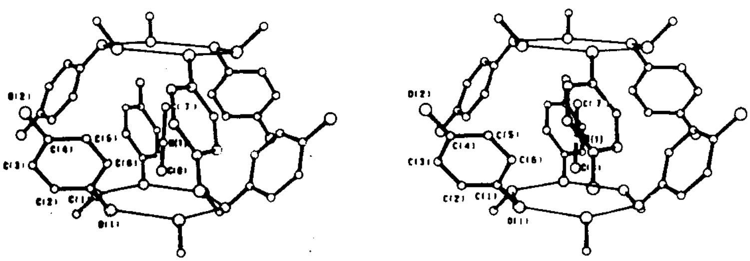

Fig. 2. A stereo-drawing showing a CH_3NC guest molecule trapped inside a cage in the structure of hydroquinone (**1**). For clarity all hydrogen atoms have been omitted. (Reproduced, by permission, from ref. 43.)

c-axis in its Type II clathrate.[43] Interesting new information has recently become available on the Type II MeOH clathrate, a system previously studied by Palin and Powell[44] using two-dimensional X-ray data. Mak,[45] employing diffractometer data, has found that the encaged MeOH molecule is located in three preferred orientations related by three-fold rotation about the c-axis, one such orientation being shown in Fig. 3. In each orientation, the C–O bond is tilted by 35° from c to facilitate interaction of the hydroxyl group with three phenolic oxygen atoms of the adjacent $[OH]_6$ ring. The inclination of 35° found above is in excellent agreement with the values of 32° below 100 K and 40° at 300 K deduced from recent dielectric studies.[46] In the MeOH clathrate, host–guest interaction is reflected in unequal OH···O hydrogen bonds in the $[OH]_6$ ring (Table 1); and, interestingly, this feature, a marked hydrogen bond length alternation, has also been found by Boeyens and Pretorius[42] in an X-ray and neutron diffraction study of the HCl clathrate

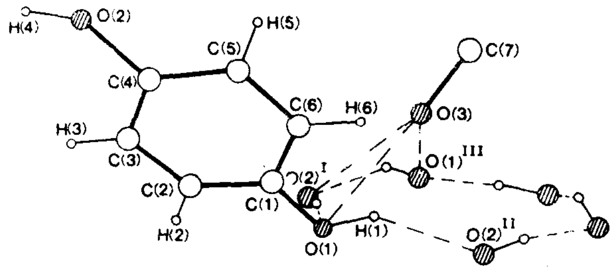

Fig. 3. *Host–guest interactions in the methanol clathrate of hydroquinone* (**1**). The O(3)–C(7) bond of the CH_3OH guest molecule is inclined at an angle of 35° to the *c*-axis of the crystal. (Reproduced, by permission, from ref. 45.)

of **1**. In this latter study the lowering of symmetry to R3 has been attributed to a large number of weak OH···Cl–H···OH interactions which orient the HCl molecule in its cage, the location of the guest being described as lying preferentially on the surface of a cone, with its generator inclined by 33° to *c* and its apex at the Cl position. The reasonable conclusion has been reached[45] that formation of Type II β-hydroquinone clathrates is favoured by guest molecules of appropriate sizes which can interact appreciably with specific sites in the walls of a clathration cavity. Very recent work[31b] has established that the SO_2 clathrate is also of Type II, and a weak interaction has been observed between the SO_2 molecule, through one of its oxygen atoms, and the $[OH]_6$ ring of the hydroquinone framework. In the acetonitrile clathrate of **1**, the only authenticated Type III system, a further lowering of symmetry from the rhombohedral lattice (R3) of Type II leads to a trigonal lattice, space group P3. There are now three distinct types of trigonal clathrate cavity and all these have the shape of prolate spheroids.[36,43] The three symmetry-independent acetonitrile molecules fit snugly inside these cavities, with, as previously suggested,[33] one guest molecule aligned in the opposite sense to the other two, see Fig. 4. Figure 5 shows electron density sections through the guest molecules; although molecule *c*, in the opposite orientation from molecules *a* and *b*, appears to be displaced from its "idealized" position along the z-axis, the disposition of this molecule with respect to the top $[OH]_6$ ring of its cage is virtually the same as that of the other molecules with respect to their bottom rings.[43] In the markedly unstable CH_3CN and CH_3NC clathrates, which rapidly lose the guest in air,[43] the mean O···O hydrogen bond lengths, 2.778 Å and 2.790 Å respectively, are significantly longer than the corresponding distances of 2.696 Å, 2.69 Å, and 2.716 Å found in the relatively stable[48] H_2S, HCl and MeOH β-hydroquinone clathrates. (There are problems in assigning an e.s.d. to the mean of quantities which are known to be unequal, Table 1.) It is intriguing