



The Golden Jubilee of Clathrates

J. ERIC D. DAVIES

Environmental Science Department, Institute of Environmental and Natural Sciences, Lancaster University, Lancaster, Lancs., LA1 4YQ, U.K.

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Abstract. 1998 is the Golden Jubilee of the introduction of the term *clathrate* by H.M. Powell. This paper traces the background to the introduction of the term.

Key words: clathrate, β -quinol, golden jubilee.

1. Introduction

The history of the preparation of compounds we now know to be *host-guest* or *supramolecular* compounds can be traced back to 1823 when Faraday [1] reported the preparation of the chlorine clathrate hydrate, and even to 1811 if we consider Davy's observations [2] to be a confirmed report. Subsequent observations of significance are the preparation of graphite intercalates [3] in 1841; the preparation of the β -quinol H₂S clathrate [4] in 1849; the preparation of cyclodextrin inclusion compounds [5] in 1891; the preparation of the nickel cyanide ammonia inclusion compound with benzene [6] in 1897; the preparation of inclusion compounds of triphenylmethane [7] in 1906; the preparation of the tri-*o*-thymotide benzene inclusion compound [8] in 1909; the preparation of clathrates of Dianin's compound [9] in 1914; the preparation of inclusion compounds of the choleic acids [10] in 1916; the preparation of phenol clathrates [11] in 1935; the preparation of urea inclusion compounds [12] in 1940 and the preparation of amylose inclusion compounds [13] in 1946.

At the time of their preparation the nature of these compounds was unknown and many of the authors commented on the fact that they seemed to be of variable composition and that in some instances the guest molecule could be removed quite easily from the compound. This latter property recalls Cronstedt's observation in 1756 that certain minerals gave the appearance of boiling on heating [14]. He called these minerals *zeo litos* (boiling stones) – the minerals now known as zeolites, the observed phenomenon being the release of the water guest molecules. With hindsight, it does seem remarkable that none of the authors was able to propose a structure for these compounds, and there is at least one instance of an X-ray study being carried out on a β -quinol clathrate with the author failing to detect the presence of the methanol guest molecule [15].

The scene was thus set for the appearance of an inspired crystallographer who was prepared to set aside the prevailing notion that all compounds should be stoichiometric, and propose a structure for these novel compounds. That crystallographer was H.M. Powell who not only proposed a structure for these compounds but also coined a new word '*clathrate*' [16] which has become an accepted part of chemical nomenclature and has gained respectability by being included in the *Oxford English Dictionary*!

As 1998 represents the Golden Jubilee of the introduction of the term *clathrate* this paper briefly outlines the history of the introduction of the term.

2. Introduction of the Term *Clathrate*

Powell's initial work concentrated on the "addition compounds of hydroquinone with certain volatile compounds". Such compounds had been known for almost a century since Wöhler's report on the H₂S compound in 1849 [4], followed by Clemm's report on the SO₂ compound in 1859 [17] and Mylius' report on the HCO₂H and HCN compounds in 1886 [18]. The first compound studied was the SO₂ compound with a preliminary report appearing in 1945 [19] and the full paper in 1947 [20]. This paper (Figure 1) reported on the detailed crystal structure of the SO₂ compound, showing how a three dimensional hydrogen bonded structure gave rise to cavities in the crystal lattice wherein the SO₂ molecules could be accommodated. The variable stoichiometry of these compounds was explained simply by the number of cavities occupied by the guest, with the maximum host:guest ratio being 3 : 1.

The term *clathrate* was not introduced until 1948 [16] when Powell published a general paper discussing the structures of these compounds (Figure 2).

The term *clathrate* is denoted as being derived from the Latin word *clathratus*: enclosed or protected by the cross bars of a grating. Although the term is now used in a wider sense, under the definition used by Powell it indicated the situation where the molecule is completely enclosed by the host and cannot escape from its surroundings.

Further information about the events leading up to the determination of the crystal structures and coining the term *clathrate* have been given by two of Professor Powell's former co-workers: S.C. Wallwork [21] and D.E. Palin [22].

3. Origin of the Term *Clathrate*

In a contribution to the inaugural issue of this *J. Incl. Phenom.* [23] Professor Powell described the circumstances behind the choice of this term:

Something was required to describe an association in which molecular imprisonment was an essential element. Because the perception of enclosure is older than man and much activity involves it – most manual action, for example – there are wide-spread works of remote ancestry for the idea. Among an

The Structure of Molecular Compounds. Part III. Crystal Structure of Addition Complexes of Quinol with Certain Volatile Compounds.

By D.E. Palin and H.M. Powell

A detailed determination, mainly by three-dimensional Fourier methods, has shown that in the compounds considered quinol molecules link together through hydrogen bonds to form infinite three-dimensional complexes of trigonal symmetry. The resulting giant molecule has a form, imposed by the dimensions of the quinol molecule and the disposition of the hydrogen bonds, so open that two such giant molecules are built up completely interpenetrating each other but having no direct attachment. In cavities enclosed simultaneously by the two giant molecules are located the molecules of the second volatile component which cannot escape from its surroundings. The composition $3C_6H_4(OH)_2 \cdot M$ is determined by the number of spaces available for the second molecule M. For the case where M is sulphur dioxide the co-ordinates of all atoms of the quinol framework have been found. The position of the sulphur dioxide and its rotation about one axis have also been established by Fourier analysis. In the quinol molecules the interatomic distances found (to within about $\pm 0.03 \text{ \AA}$) are C-C 1.39, C-O 1.36, OH...O 2.75 \AA . The hydroxyl groups are arranged in hydrogen-bonded hexagons. The analysis involves some special applications of Patterson methods which here are able to establish the presence of a symmetry centre and to locate most of the atoms in a direct manner.

Figure 1. The abstract from the paper [*J. Chem. Soc.* **208** (1947)] reporting the crystal structure of the quinol/SO₂ compound.

The Structure of Molecular Compounds. Part IV. Clathrate Compounds.

By H.M. Powell.

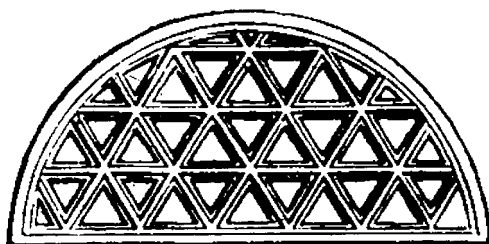
It is shown that molecules may be firmly united to each other without the operation of strong attractive forces between them but through the enclosure of one by the other, of both by each other, or in more complex ways. The space arrangements are such that it is impossible to separate the different components without overcoming the strong attachment, e.g., by hydrogen bonds of the molecules of one component only which are thus joined to form an enclosing structure around the others. The conditions of formation, the compositions, and some properties of such compounds are discussed. Among the examples given are those in which either two or more identical giant molecules interpenetrate and enclose each other, and others in which cage structures of suitable form imprison molecules of a second kind to give compounds of either fixed or variable molecular ratios. It is suggested that they should be named "clathrate compounds" ("clathratus," enclosed or protected by cross bars of a grating)

Figure 2. The abstract of the paper by Powell [*J. Chem. Soc.* **61** (1948)] introducing the term *clathrate*.

international profusion that have the general form of a vowel clutched between some form of KL and a HISS was one happily provided by my former school. The mementoes included a dictionary, first published a few years after Clemm made the sulphur dioxide clathrate, concerning the industrial arts and social life of the Greeks and Romans. It gave the meaning of *clathratus* as "closed or protected by the cross bars of trellis". The *clathri* "enclose anything gener-

CLATHRA'TUS. Closed or protected by cross-bars of trellis (*clathri*), as explained in the next paragraph. Plaut. *Mil.* ii. 4. 25.

CLA'THRI. A *trellis* or grating of wood or metal employed to cover over and protect an aperture, such as



a door or window, or to enclose anything generally. (Hor. *A. P.* 473. Plin. *H. N.* viii. 7. Cato, *R. R.* iv. 1. Columell. viii. 17. 10.) The example represents the trellis which covered in the lunettes over the stalls (*carceres*) in the circus of Caracalla.

Figure 3. Entries in *A Dictionary of Roman and Greek Antiquities* (A. Rich, Longmans Green, London, revised 1884).

ally". A wood engraving illustrated the trellis which covered the lunettes over the stalls (*carceres*) in the circus of Caracalla (Figure 3).

4. Perspective

Powell and his co-workers studied the quinol clathrates extensively and obtained detailed information on systems containing both molecular and monatomic guests – the latter being, at the time, unusual examples of compounds containing rare gas atoms. As indicated in the Appendix his group also solved the structures of clathrates formed by the nickel ammonia cyanide host, tri-*o*-thymotide and Dianin's compound. His work thus established the true nature of host–guest compounds and formed the firm foundation on which subsequent interdisciplinary work on supramolecular chemistry is based [24]. Professor Powell died in 1991 [25] and thus witnessed the final accolade for his work *viz* the award of the 1987 Nobel Prize in Chemistry to Professors Cram, Lehn and Pedersen.

Appendix

H.M. POWELL'S PUBLICATIONS ON CLATHRATES

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- D.E. Palin and H.M. Powell: *J. Chem. Soc.* 208 (1947). 'The Structure of Molecular Compounds. Part III. Crystal Structure of Addition Complexes of Hydroquinone with Certain Volatile Compounds'.
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