Supramolecular Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

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To cite this Article Udachin, K. A. , Ratcliffe, C. I. , Enright, G. D. and Ripmeester, J. A.(1997) 'Structure H Hydrate: A Single Crystal Diffraction Study of 2,2-dimethylpentane·5(Xe, H_2S)·34H_2O', Supramolecular Chemistry, 8: 3, 173 — 176
To link to this Article: DOI: 10.1080/10610279708034933
URL: http://dx.doi.org/10.1080/10610279708034933

SUPRAMOLECULAR CHEMISTRY, 1997, Vol. 8, pp. 173–176
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Communication

Structure H Hydrate: a Single Crystal Diffraction Study of 2,2-dimethylpentane·5(Xe, H_2S)·$34H_2O$

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Published as NRCC no. 39124

(Received 20 August 1996)

Although Structure H hydrate has been studied intensively for a number of years, its detailed crystal structure has remained unknown. Single crystal X-ray diffraction was used to determine the structure of 2,2-dimethylpentane·5(Xe, H_2S)·$34H_2O$ hydrate. The hexagonal unit cell, space group *P6/mmm* with z=1, has the following parameters: $a=12.212(2)$, $c=10.143(2)$ Å (t=−100°C). Cage geometries and fractional coordinates for the atoms are presented and discussed. Structure H hydrate is only the third hydrate type for which a large number of molecules are suitable as guests.

Until 10 years ago it was believed that there were only two major structural types of clathrate hydrates, cubic Structures I and II with similar small cages (5^{12})# and different large cages ($5^{12}6^2$—I, $5^{12}6^4$—II)[1–6]. About 120 guest species suitable for these structures have been identified[5,6]. Over the years hydrates with natural gas components as guests have been a subject of many investigations, as natural gas hydrates were known to block gas transmission lines[7]. More recently a great deal of interest in natural gas hydrates has been provoked by the discovery of vast natural gas hydrate deposits both on- and off-shore[8]. These have potential as an energy resource, they have been proposed to be agents of climate change, and also they have a known role as industrial and geological hazards[8].

The largest natural gas component suitable for the structure II large cage was thought to be n-butane. Then it was discovered that in the presence of small "help-gas" molecules certain molecules too large to fit into any of the known cages appeared to be forming hydrates. NMR spectroscopy was used to define the cage shapes and relative sizes for the new structure, and powder diffraction was used to determine the Laue symmetry[9]. By analogy, the new hydrate structure was proposed to be isostructural with the clathrasil Dodecasil-1H[10], and was termed

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Structure H. Subsequently, about 30 new guests suitable for the large cage in structure H were identified, including many hydrocarbons such as methyl-substituted butanes and pentanes, cycloalkanes and methyl-substituted cycloalkanes, and cage molecules such as adamantane[11]. It was also shown that with a help-gas, structure H hydrate forms in hydrocarbon liquids such as naphtha and gasoline[12].

It is now recognized[13] that Structure H may be a significant contributor to gas hydrate formation where some of the higher hydrocarbons are significant components, and thus it is very important to develop a good model for its thermodynamic stability. Much effort has already been expended in phase equilibrium studies[14] and model development based on the proposed structure. However, the structural model, first of all, requires confirmation, and accurate atomic positions are needed for the development of interaction potentials. The ability to predict conditions of stability is important for the exploration and exploitation of natural gas hydrates and also the prevention of gas hydrate blockage in pipelines. In this paper we present the first single crystal X-ray diffraction study of a Structure H hydrate and confirm that the surmised structure is indeed correct.

Crystals were grown in a sealed tube from the four phase mixture of 2,2-dimethylpentane, Xe, H_2S and ice at approximately −20°C for 6 years. On the walls of the sealed tube there formed transparent well-edged hexagonal prisms of the hydrate 2,2-dimethylpentane·5(Xe, H_2S)·$34H_2O$. The decomposition temperature of the hydrate in the sealed tube was 0.6°C. The hydrate single crystal (size 0.3×0.4×0.6 mm) was placed into a thin-wall glass capillary at −80°C and analyzed by X-ray diffraction techniques. We carried out the experiment on a Siemens diffractometer with a CCD detector using Mo K_α radiation and a graphite monochromator. The hexagonal unit cell of the hydrate has the following parameters: $a=12.212(2)$, $c=10.143(2)$ Å, $(t=-100°C)$, the space group $P6/mmm$, $z=1$, and $\rho_{calc}=1.291$ g·cm^{-3}. Solution and refinement of the structure was carried out with the help of the program described in ref. 15. For 432 ($I > 2.5\sigma(I)$) observed (5043 total) reflections, the structure was refined to $R = 0.025$ ($R_w = 0.055$). Xenon and oxygen atoms were refined with anisotropic thermal parameters. The hydrogen atoms of the water molecules were located on a Fourier difference map. Table I lists the fractional coordinates.

The compound studied is a classic clathrate hydrate structure, which means that there are no interactions between the host and guest molecules other than van der Waals interactions. A general view of the water framework is presented on Fig. 1. The water framework consists of one large E (= Eicosahedron) cavity ($5^{12}6^8$) and two types of small cavities D (= dodecahedron) cavities D (5^{12}), and D′ ($4^35^66^3$). These are the first examples of both the D′ and E cages in true clathrate hydrate structures. In general, the possibility of having square faces should expand

TABLE I Atomic coordinates and isotropic displacement parameters

	x	y	z	B_{iso}
O1	0.79099(6)	0.20901	0.27765(13)	2.27(4)
O2	0.66667	0.33333	0.36433(23)	2.17(7)
O3	0.61389(12)	0.61389	0.13726(13)	2.39(5)
O4	0.86798(8)	0.13202	0.50000	2.26(7)
Xe1	0.66667	0.33333	0.00000	1.99(3)
Xe2	0.50000	0.50000	0.50000	1.99(3)
E cavity center	0.00000	0.00000	0.00000	

B_{iso} is the mean of the principal axes of the thermal ellipsoid.

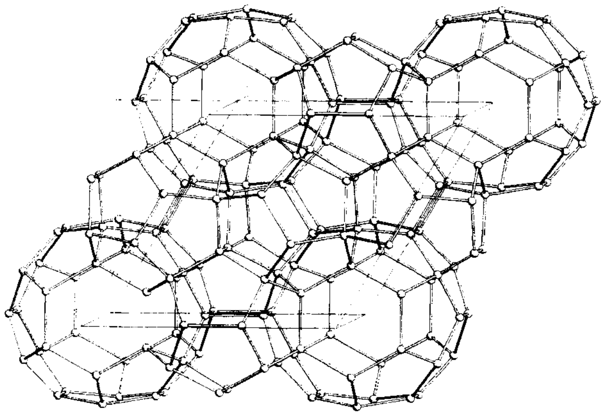

FIGURE 1 Water framework of structure H as viewed approximately along the axis *c*. Hydrogen atoms are omitted.

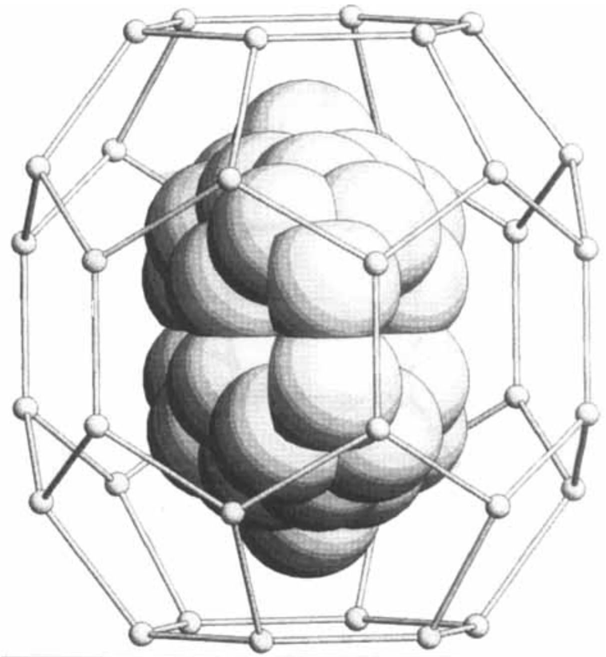

FIGURE 2 Molecule of of 2,2-dimethylpentane disordered in large cavity $5^{12}6^{8}$. Hydrogen atoms are omitted.

the scope of possible hydrate structures considerably. We note that structure H was not one of the hydrate structures considered by Jeffrey in his review of known and potential structures[16].

The lengths of the hydrogen bonds $O_w...O_w$ in the water framework vary from 2.77 to 2.79 Å, and the angles $O_w...O_w...O_w$ between the hydrogen bonds in the water framework vary from 90.0 to 120.7°. Thus, the requirements of a tetrahedral arrangement of the hydrogen bonds in water molecules are not met very well. The 2,2-dimethylpentane molecule is situated in the large cavity which has 6/mmm symmetry (Fig. 2) and is disordered about the 6-fold axis of the cage. Xe and H_2S molecules occupy the small D and D′ cavities. The dodecahedral cavity D has a *mmm* symmetry, and cavity D′ has a symmetry of $-6m2$. The guest molecules fit well into the cavities of the structure.

Parameters which characterize the free volume of the cavities are given in Table II. The intermolecular distances between Xe (or S) and water molecules are 3.90–3.95 Å. The intermolecular distances between 2,2-dimethylpentane and water molecules are $C...O_w = 3.19–3.47$ Å. The hydrogen atoms are disordered and were refined as 1/2 H's at two sites within each O-H--O hydrogen bond (Fig. 3). The H-O distances are 0.98–1.01 Å and the angles $H\text{-}O_w\text{--}H$ equal 100.9–119.8°.

As pointed out previously[9,11], Structure H hydrate is expected to be the largest hydrate structural group, as any hydrophobic molecule with appropriate space-filling properties for the E cage (van der Waals' diameters between about 7.0 and 8.5 Å) should be suitable as guest. For all of the hydrocarbon guests for which it was shown explicitly that structure H hydrate is formed it should be possible to substitute at least one methyl group per molecule by OH, SH, Br or I, from one to all methyl groups per mole-

TABLE II Approximate axes (Å) of the ellipsoidal free volume available for the guests in the structure H cavities

Cavity	a	b	c
H	6.84	6.84	8.58
D′	5.06	5.06	4.40
D	4.86	4.88	4.56

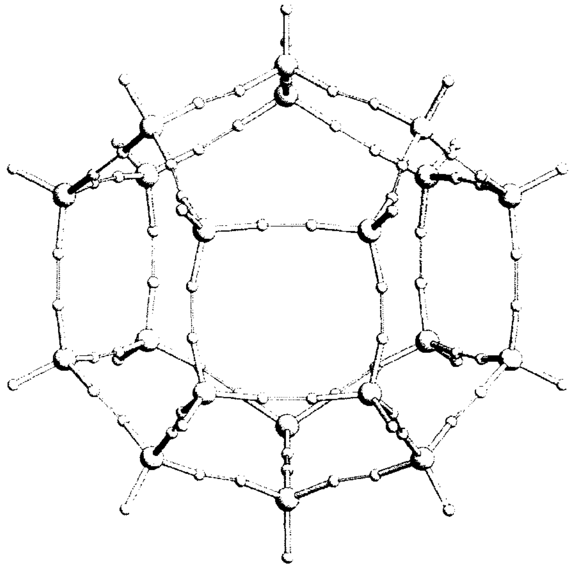

FIGURE 3 Disordering of hydrogen atoms in water framework of structure H (small D'-cavity).

cule with F or Cl, and at least one CH_2 group per molecule by O, S or C=O. Various combinations and permutations of these substitutions are also possible, giving a very large number of possible guests.

Acknowledgments

KAU and CIR thank the NATO Science Program for the award of a Collaborative Research Grant.

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Endnotes

\# The x^y descriptor designates the number, y, of polyhedral faces of type x present in each cage.