

Hydrate Inclusion Compounds

G. A. JEFFREY

Department of Crystallography, University of Pittsburgh, Pittsburgh, PA 15260, U.S.A.

(Received: 7 March 1983)

Abstract. There are three general classes of hydrate inclusion compounds: the 'gas' hydrates, the per-alkyl onium salt hydrates, and the alkylamine hydrates. The first are clathrates, the second are ionic inclusion compounds, the third are 'semi-clathrates'. Crystallization occurs because the H_2O molecules, like SiO_2 , can form three-dimensional four-connected nets. With water alone, these are the ices. In the inclusion hydrates, nets with larger voids are stabilized by including other 'guest' molecules. Anions and hydrogen-bonding functional groups can replace water molecules in these nets, in which case the 'guest' species are cations or hydrophobic moieties of organic molecules. The guest must satisfy two criteria. One is dimensional, to ensure a 'comfortable' fit within the voids. The other is functional. The guest molecules cannot have either a single strong hydrogen-bonding group, such as an amide or a carboxylate, or a number of moderately strong hydrogen-bonding groups, as in a polyol or a carbohydrate.

The common topological feature of these nets is the pentagonal dodecahedra: i.e., 5^{12} -hedron. These are combined with $5^{12}6^2$ -hedra, $5^{12}6^3$ -hedra, $5^{12}6^4$ -hedra and combinations of these polyhedra, to form five known nets. Two of these are the well-known 12 and 17 Å cubic gas hydrate structures, $Pm3n$, $Fd3m$; one is tetragonal, $P4_2/mmm$, and two are hexagonal, $P6_3/mmc$ and $P6/mmm$. The clathrate hydrates provide examples of the two cubic and the tetragonal structures. The alkyl onium salt hydrates have distorted versions of the $Pm3n$ cubic, the tetragonal, and one of the hexagonal structures. The alkylamine hydrate structures hitherto determined provide examples of distorted versions of the two hexagonal structures.

There are also three hydrate inclusion structures, represented by single examples, which do not involve the 5^{12} -hedra. These are $4(CH_3)_3CHNH_2 \cdot 39H_2O$ which is a clathrate; $HPF_6 \cdot 6H_2O$ and $(CH_3)_4NOH \cdot 5H_2O$ which are ionic-water inclusion hydrates. In the monoclinic $6(CH_2CH_2CH_2NH_2) \cdot 105H_2O$ and the orthorhombic $3(CH_2CH_2)_2NH \cdot 26H_2O$, the water structure is more complex. The idealization of these nets in terms of the close-packing of semi-regular polyhedra becomes difficult and artificial. There is an approach towards the complexity of the water salt structures found in the crystals of proteins.

Key words: hydrate inclusion compounds, crystal structures, clathrate hydrates, gas hydrates, alkylamines, water molecules.

1. Introduction

Water molecules have the unique property that, in association with other water molecules, each can form four tetrahedrally-disposed hydrogen bonds, half of which are donors and half acceptors. For this reason, water can form polymeric three-dimensional, four-connected network structures [1]. The topological problem of cataloging *all* the possible three-dimensional, four-connected nets has not, to my knowledge, been solved. At least not in a way that is useful to the structural chemist. So we cannot be sure for example that all the possible polymorphs of ice have now been discovered [2]. Nor can we predict how many hydrate inclusion structures, which are three-dimensional four-connected nets with larger voids than the ices, will be discovered in the future.

Possibly because water is so cheap and commonplace in those parts of the world that are wealthy enough to afford the luxury of sustaining some small amount of scientific research, for the sake of curiosity alone, water has never been given the attention that its solid state

chemistry deserves. Research into the preparation, properties and structure of hydrates in which the water molecules are the majority and structure determining species has had a history that can only be described as spasmodic.

The gas hydrates invoked a relatively large amount of scientific curiosity in the nineteenth century. Most of the clathrate hydrates now known were prepared and identified prior to 1900, with the exception of those of the more complex halogenated hydrocarbons, cyclic ethers and imines. The hydrocarbon hydrates were the target of considerable applied research in the 1930s in the mid U.S. states because of their nuisance properties in natural gas transmission pipe lines. They were studied again in the 1940s in Germany because of their possible relevance to the storage and transport of hydrocarbon fuels. Lastly, in the 1960s the refrigerant gas hydrates were studied because of the industrial potential of a clathrate hydrate desalination process.

The work prior to 1925 is described in a very comprehensive review article [3] which provides about 300 references to the research which followed Davy and Faraday's [4] discovery of the chlorine hydrate in 1811.

The more technological research relating to natural gas pipeline problems was reviewed very comprehensively in 1948 [5]. The discovery of the other two major groups of hydrate inclusion compounds, the alkylamine hydrates and the quaternary ammonium salt hydrates, resulted from investigations aimed more at understanding the properties of aqueous solutions than at advancing the knowledge of the solid state chemistry of water. Pickering's remarkable 1893 paper [6] is entitled 'The Hydrate Theory of Solutions'. Kraus, who – with his collaborators – discovered the tetra-*n*-butyl and tetra-*iso*-amyl ammonium salt hydrates [7], was a physical chemist primarily interested in the thermodynamics of the solutions of these compounds. Jeffrey and McMullan's work [8] on the crystal structures of the quaternary alkyl ammonium salt hydrates was prompted by the curiosity of a physical chemist, Henry Frank, whose primary interest was in the thermodynamics of aqueous solutions.

Until Powell discovered the phenomenon of molecular association by clathration [9], there was no basis for understanding why crystalline compounds should exist with such exotic chemical formulae, as



This question would not concern the nineteenth-century chemists because prior to valence theory, the compositions of the gas hydrates, which were thought at that time to be much simpler, were no more inconsistent with current thought about chemical composition than any other chemicals. It was not until after the development of the highly successful electronic theories of Lewis and Sidgwick, that crystalline compounds formed by the association of valence-saturated molecules with fully completed octets of electrons were recognized as misfits. These compounds then suffered the fate of most misfits, by being benignly ignored for many years.

Powell's research on the quinol-SO₂ clathrate, provided the essential clue. The two clathrate hydrate structures, which encompass the majority of structures of the gas hydrates, were determined simultaneously by three investigators a few years later [10]. The connection between these structures and the alkylamine hydrates and quaternary ammonium salt hydrates was not known, or suspected, until these structures were investigated by X-ray structure analysis, nearly ten years later [11]. It is interesting to note, however, that Schroeder included Pickering's work in his 1925 review of the chemistry of the gas hydrates.

2. The Gas Hydrates

The characteristic feature of the gas hydrate water structures is the $H_{40}O_{20}$ pentagonal dodecahedron, with its 12 pentagonal faces, 5^{12} , 20 vertices, and 30 edges shown in Figure 1. Thirty of the 40 hydrogen atoms form the hydrogen bond edges, leaving 10 hydrogen atoms for distribution amongst the 20 vertices, 10 of which act as donors and 10 as acceptors to adjacent water molecules. When these polyhedra are linked together, each water molecule is four-coordinated in the same donor/acceptor ratio as in ice with a geometry which is close to tetrahedral. Unlike other polyhedra familiar to solid state chemists, i.e., the tetrahedron, octahedron and the icosahedron, the pentagonal dodecahedron, shown in Figure 2, cannot

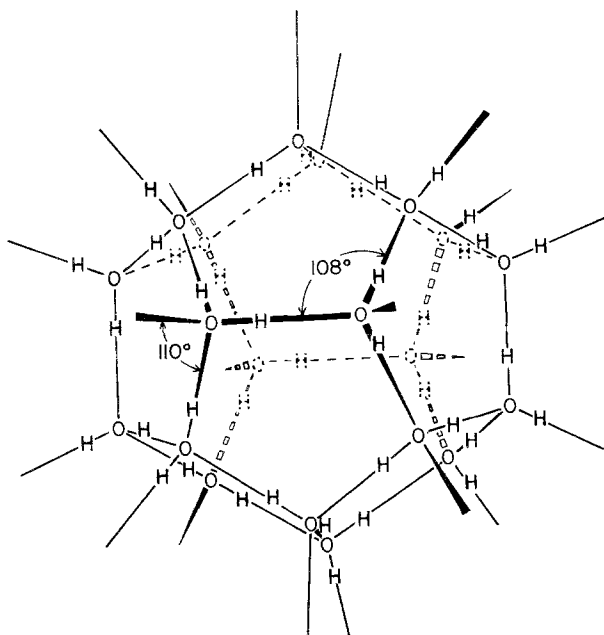


Fig. 1. The $H_{40}O_{20}$ pentagonal dodecahedron. This shows one of the ordered arrangements of the hydrogen atoms. In the gas hydrates the hydrogen atoms are twofold disordered across the O---O edges.

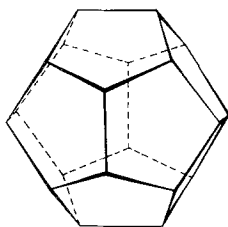


Fig. 2. The 12-hedra, 5^{12} .

fill space in any face-sharing periodic arrangement. Different polyhedra are necessary to provide the three-dimensional repeating patterns necessary for a crystal structure. When the pentagonal dodecahedra are joined, either by separate links or by sharing faces, other different

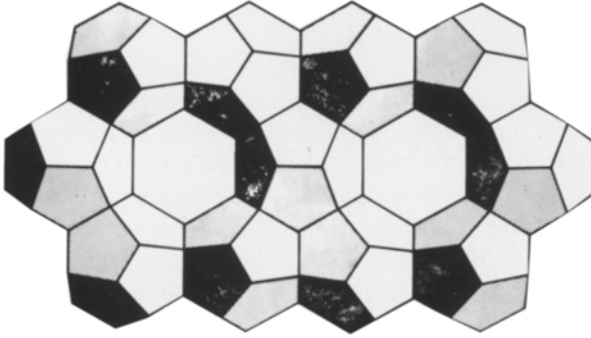


Fig. 3. The pattern formed by face-sharing the 12-hedra into layers. The hexagonal faces can belong to 13-, 14- or 16-hedra.

polyhedra are generated, as illustrated in Figure 3. (Linking by sharing edges is inconsistent with the four-coordinated water geometry and the retention of a three-dimensional four-connected net.) When the other polyhedra are the 14-hedra, with 12 pentagons and two hexagons, $5^{12}6^2$, shown in Figure 4, or the 16-hedra, $5^{12}6^4$, with 12 pentagons and four hexagons shown in Figure 5, the two main types of gas hydrate water clathrate structures are formed by a face-sharing arrangement of these polyhedra into three-dimensional patterns that have cubic symmetry. These are commonly referred to as the Type I, 12 Å, cubic $Pm\bar{3}n$ structure, and the Type II, 17 Å, $Fd\bar{3}m$ structure. These are by no means the only possible arrangements involving the pentagonal dodecahedron, but as far as we know, the only two which have cubic symmetry. In these water structures, each oxygen atom is four-coordinated by hydrogen bonds in a nearly tetrahedral arrangement. These structures would be stable ice polymorphs were it not for the fact that the mean diameters of the 12-, 14- and 16-hedra are 7.8, 8.6 and 9.4 Å, respectively. At this distance, the van der Waals forces across the diameters of the voids are sufficiently attractive to cause a collapse of the relatively weak hydrogen-bonded framework structure. To stabilize these structures, it is necessary to fill the voids with molecules which do not compete or interfere with the hydrogen bonding of the clathrate water structure. Any molecule will do the trick, providing it has the appropriate dimensions to fit comfortably 'van der Waals-wise' within the voids and it does not have strong hydrophilic properties.

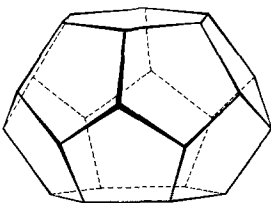


Fig. 4. The 14-hedra, $5^{12}6^2$.

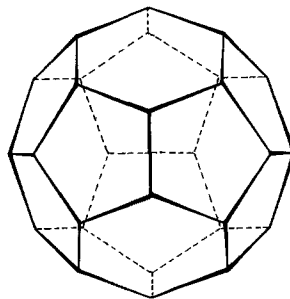
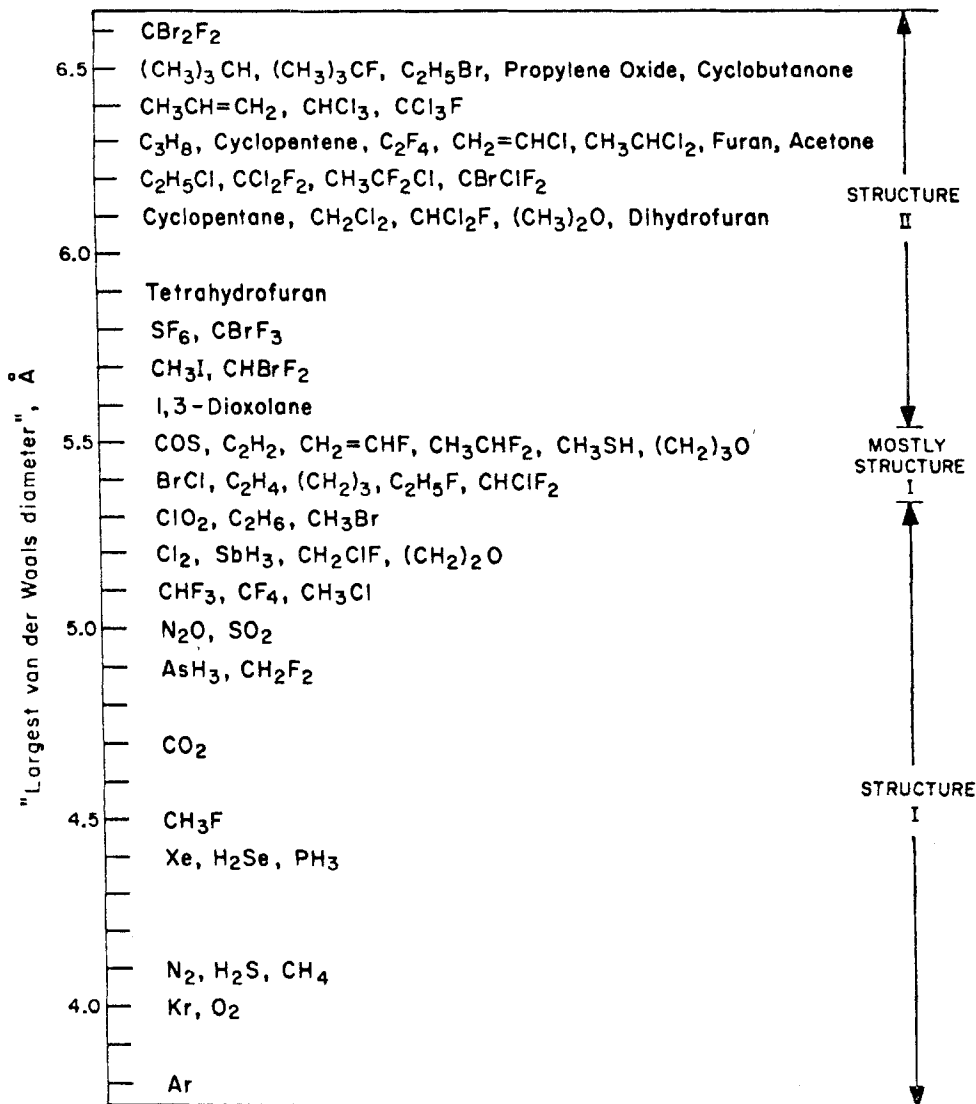


Fig. 5. The 16-hedra, $5^{12}6^4$.

Table I. Molecules which form Types I and II gas hydrates (from D. W. Davidson, Chapt. 3 in 'Water: A Comprehensive Treatise', Vol. 2 (Ed. F. Franks), Plenum Press, (1973)).



A list of molecules which form clathrate hydrates is shown in Table I. This includes cyclic imines, ethers and ketones, but not the polyols or strong acids. It is necessary to fill the larger 14- and 16-hedra to form stable crystals, but the 12-hedra need only be partially filled, for example by the accidental inclusion of air molecules. Deliberate inclusion, by bubbling in H₂S as a 'help-gas', raises the decomposition temperature of the hydrate. This can be demonstrated simply by bubbling H₂S into an agitated mixture of water and carbon tetrachloride to produce a white precipitation of the H₂S, CCl₄ double hydrate. CCl₄ can only occupy the large 16-hedra and H₂S goes into the smaller 12-hedra.

Bromine hydrate is an interesting structure in that it is one of the few clathrate hydrates that does not have one or both of the two cubic structures. Although it was first prepared

in 1829 [12], its structure is still not absolutely certain. There is good evidence that it has a tetragonal structure, $P4_2/nmn$ [13], formed by 12-hedra, 14-hedra and the 15-hedra shown in Figure 6. Ethanol is also reported to form two hydrates, one of which may be the tetragonal form [14]. Again, this is a preliminary unconfirmed result that requires further investigation.

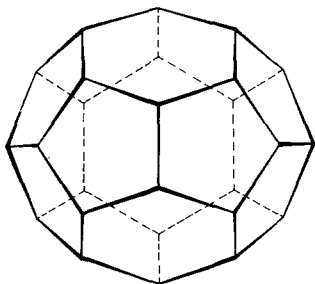


Fig. 6. The 15-hedra, $5^{12}6^3$.

3. The Alkylamine Hydrates

Pickering in 1893 [6] reported phase data for about 30 amine hydrates. Somerville in 1931 [15] and, in recent years, Carbonnel and her collaborators [16] have been adding some very careful phase studies for both these hydrates and the clathrate hydrates of various cyclic ethers, imines and more complex organic molecules. Glew [17] reanalyzed some of the earlier phase diagram data on the alkylamine hydrates and proposed that these structures were related to those of the gas hydrates. Nine of the alkylamine hydrates have been characterized crystallographically [18] and for five of them, complete X-ray structure analyses were carried out [19]. These structures are indeed related to those of the gas hydrates, but with one exception, they are not true clathrates. This is because the alkylamine molecules hydrogen bond to the water framework through their amine group. For this reason, they were described as 'semi-clathrates' [19]. The structures of those that were analyzed are more complex than those of the gas hydrates and, unlike the gas hydrates, every amine so far examined has a different water structure.

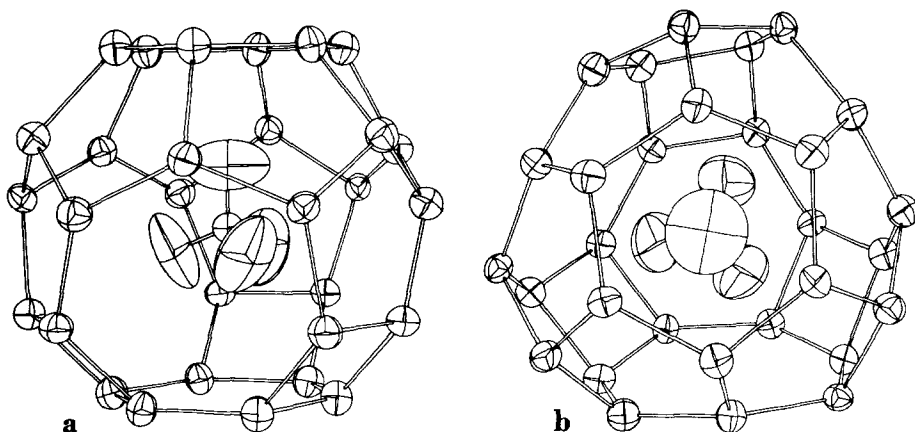


Fig. 7. The *t*-butylamine clathrate hydrate, $16(\text{CH}_3)_3\text{CNH}_2 \cdot 156\text{H}_2\text{O}$. The 17-hedra is $7^3 6^2 5^9 4^3$. (a) View normal to the C-N bond; (b) View down the C-N bond and the threefold axis.

The amine hydrate which is a true clathrate is that of *tert*-butylamine, $16(\text{CH}_3)_3\text{CHNH}_2 \cdot 156\text{H}_2\text{O}$ [20], which occupies the 17-hedra, with square pentagonal, hexagonal and heptagonal faces, $4^35^96^27^3$, shown in Figure 7. This is not a space-filing polyhedron, and the residual voids are octahedral with square and pentagonal faces, 4^45^4 . These small voids appear to be vacant. They are, in fact, comparable in size to the voids in the normal hexagonal ice structure. It is surprising that this primary amine is a nonbonded molecule in the water structure, whereas the tertiary amine, trimethylamine, in $4(\text{CH}_3)_3\text{N} \cdot 4\text{H}_2\text{O}$ is a semi-clathrate, with the nitrogen atom accepting a hydrogen bond from the water framework [21].

In the semi-clathrate amine hydrate structures, the functional group forms part of the hydrogen-bonded water framework, while the alkyl chains function to stabilize the voids, as do the hydrocarbon molecules in the gas hydrates. The structures are more complex and the distortions from equal edges and tetrahedral coordination at the vertices are greater than in the gas hydrate structures. In the most complex of the alkylamine hydrates studied, that of the low temperature modification of the *n*-propylamine hydrate, $16\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH}_2 \cdot 104\text{H}_2\text{O}$ [22], the distortions became so severe that rationalization of the water structure in terms of face-sharing polyhedra became very idealized. The water structure consists of a large concave polyhedron of about 2200 Å with convex compartments which have pentagonal and hexagonal faces, but are difficult to rationalize in terms of complete polyhedra.

4. The Quaternary Ammonium Salt Hydrates

The hydrates are formed by the salts of tetra-*n*-butyl or tetra-*iso*-amyl groups on a quaternary ammonium or phosphonium cation. They are also formed by salts with three of these alkyl groups on a sulphonium cation. The polyhedra voids are 44-, 45- and 46-hedra which can be constructed from combinations of 14-, 15- and 16-hedra as illustrated in Figures 8, 9 and 10.

The cations fulfill the void-filling role of the gases in the gas hydrates. The anions are hydrogen-bonded with the water molecules to form part of the clathrate cage structure, as are the amine groups in the semi-clathrates. These compounds are therefore ionic rather than molecular inclusion compounds [8]. A typical example of the cationic inclusion is shown in Figure 11. The water-anion cages are necessarily distorted relative to those of the gas hydrates, but the similarities between the two types of structures are very close for the 12 Å cubic $Pm3n$ type of structure [23]. The other major gas hydrate type, the 17 Å cubic $Fd3m$ structure

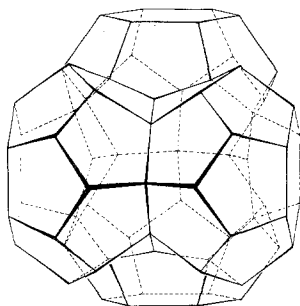


Fig. 8. 44-Hedron, $5^{40}6^4$, formed from four 14-hedra.

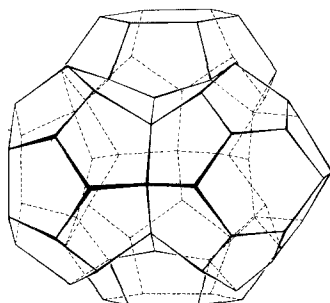


Fig. 9. 45-Hedron, $5^{40}6^5$, formed from three 14-hedra and one 15-hedra.

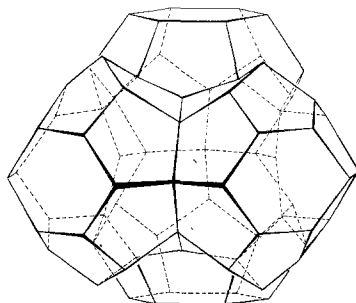


Fig. 10. 46-Hedron, $5^{54}6^6$, formed from two 14-hedra and two 15-hedra.

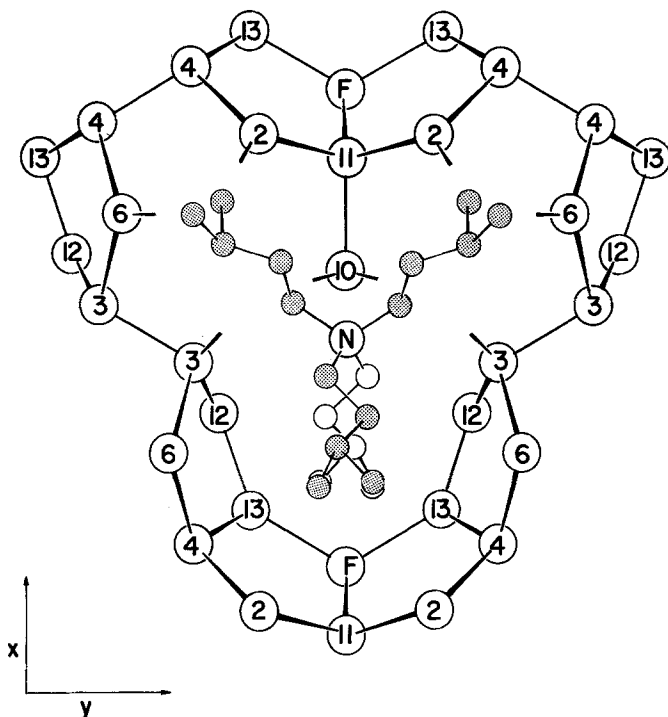


Fig. 11. A tetra-iso-amyl ammonium cation included in the distorted 46-hedron in the structure of $(i\text{-C}_5\text{H}_{11})_4\text{NF} \cdot 38\text{H}_2\text{O}$.

is not represented in this series, but the tetragonal $P4/mnm$ structure (that postulated for bromine hydrate) is represented [24].

Taking these three major types of hydrate inclusion compounds as a group, six types of inclusion structures can be identified. A seventh related structure is that of hexafluorophosphoric acid [25], $2\text{HPF}_6 \cdot 12\text{H}_2\text{O}$ which is based on face-shared cubic octahedra, $4^6 6^6$. This is a space-filling polyhedron requiring no additional polyhedra to form a three-dimensional periodic pattern. The polyhedral relationship of these seven types is shown in Table II.

5. Related Structures

The silicates also form three-dimensional, four-connected nets in which the Si atoms are the vertices and the Si–O–Si bonds are the edges. Therefore, analogues of the clathrate hydrate structures can be expected in both natural and synthetic minerals, as is indeed the case [26,27].

Any Group IV element, or III/V, II/VI binary compounds, can also form these structures with covalent bonds as the edges. No examples are yet reported for carbon, but silicon forms a series of metal silicates in which the metal atoms are the included species [28]. Both the 12 and 17 Å cubic structures are represented. Germanium arsenide forms a compound with the 12 Å cubic structure with the formula $(\text{Ge}_{38}\text{As}_8)^{8+} 8\text{I}^-$ [29]. This is a cationic clathrate structure with an anionic included species, which could well be the first example of a new series of inclusion compounds of technological interest which have clathrate hydrate-like structures with covalent bonds, rather than hydrogen bonds, forming the three-dimensional frameworks.

Table II. The polyhedral relationships between the hydrate inclusion compounds

		5^{12} +					
		$5^{12}6^4$		$5^{12}6^2 + 5^{12}6^3$		$4^45^4 + 4^35^96^{2\cdot7^3}$	
		Cubic 17 Å	Hexagonal 19 Å 12 Å	Tetragonal 12 Å 24 Å	Hexagonal 12 Å 12 Å	Cubic 19 Å	Cubic 8 Å
$5^{12}6^2$	Cubic 12 Å						
	$6X \cdot 2Y \cdot 46H_2O$	$8X \cdot 16Y \cdot 136H_2O$	$[4X \cdot 8Y \cdot 68H_2O]$	$[20X \cdot 10Y \cdot 172H_2O]$ $4R_4N^+A^-158H_2O$ $5R_4N^+A^-164H_2O$	$[8X \cdot 6Y \cdot 80H_2O]$	$16(CH_3)CHNH_2 \cdot 156H_2O$	$2HPF_6 \cdot 12H_2O$
	$2R_3S^+A^-40H_2O$	-	-	-	-	-	-
	$[6CH_3CH_2NH_2 \cdot 46H_2O]$	-	$10(CH_3)_2CHNH_2 \cdot 80H_2O$	-	$4(CH_3)_3N \cdot 41H_2O$	-	-
	$[6(CH_3)_2NH_2 \cdot 52H_2O]$	-	-	-	-	-	-
	Cubic 24 Å						
	$[6R_4N^+A^-344H_2O]$						
					Orthorhombic		
					$2R_4N^+A^-76H_2O$		
					Monoclinic		
					$2R_3S^+A^-46H_2O$		

6. Future Possibilities

There are clearly many more alkylamine hydrates that are either true clathrates or semi-clathrates. It is likely that the majority of these will represent new types of inclusion structures. This is crystallographically difficult research, and the investigators tend to become socially unpopular after prolonged exposure to the preparation and handling of these compounds. The gas hydrate and quaternary alkyl cationic hydrates have been more thoroughly explored and it is possible to predict with some degree of certainty whether a particular molecule or salt will form an inclusion hydrate.

Does this exhaust the extent of the hydrate inclusion compounds or can we anticipate discoveries of whole new classes? Since ethanol and the alkylamines form hydrate inclusion compounds, why not methanol and other aliphatic alcohols?

A limited amount of structural work has been done on the higher hydrates of the diamines and diols. When the two functional groups are separated by short hydrocarbon chains, the functional groups and the water molecules form clathrate-like framework structures as found in pinacol hexahydrate [30] and piperazine hexahydrate [31] shown in Figure 12. The water and hydroxyl groups form hydrogen-bonded layers of buckled pentagons shown in Figure 13.

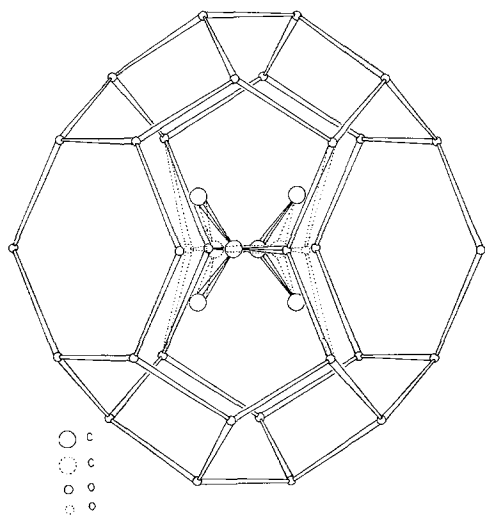


Fig. 12. Pinacol molecule in a hydrogen-bonded hydrate-hydroxyl void in CH_2 . The dotted lines indicate an alternate disordered position.

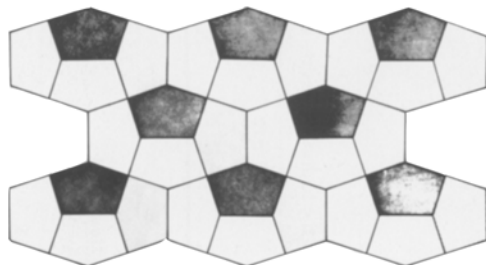


Fig. 13. Pattern of buckled pentagons of hydrogen-bonded oxygens observed in the pinacol and piperazine hexahydrates and in dimethyl hexanediol and octanediol tetrahydrates.

When the hydrocarbon chains are longer, layer structures are formed [32] in which the water molecules and the functional groups form puckered layers of edge-sharing pentagons as shown in Figure 14. The preference of water molecules for the pentagon in the solid-state topology, which dominates the clathrate hydrate structures, is clearly apparent in these structures also. It will probably require some technological resurgence of interest in these hydrate inclusion materials to spark the next major research effort in this field; just curiosity is not enough.

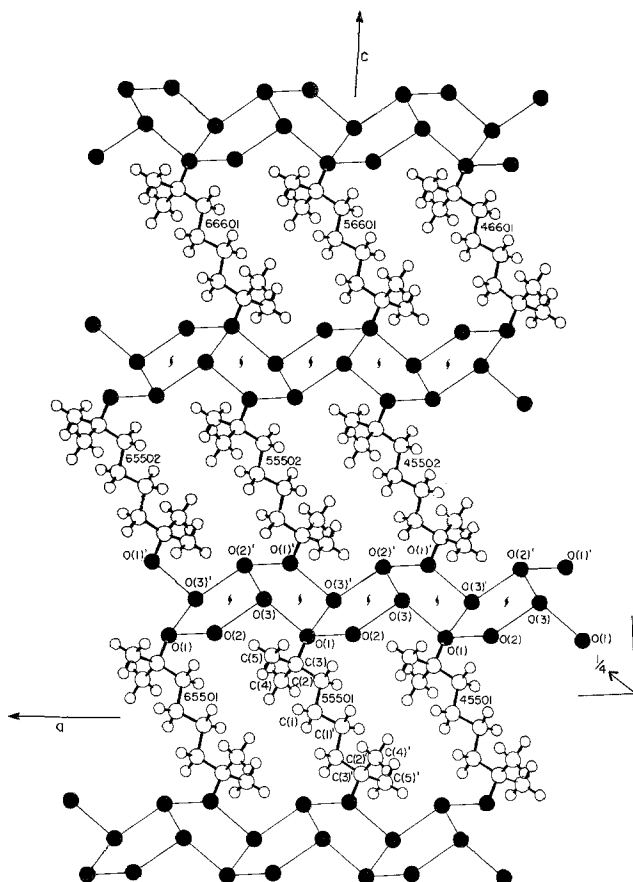


Fig. 14. The hydrocarbon-water 'sandwich' structure in 2,7-dimethyl-2,7-octanediol tetrahydrate.

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