

Commentationes

Chemical Applications of Topology and Group Theory VI. Polyhedral Water Networks in Clathrates and Semiclathrates

R. B. KING

Department of Chemistry, University of Georgia, Athens, Georgia 30601, USA

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Possible convex polyhedra for three-dimensional water networks in clathrate and semiclathrate hydrates are discussed in this paper. All such polyhedra have all vertices of order three. Therefore, the number of vertices (v), edges (e), and faces (f) must satisfy the equalities $e = 3v/2$ and $f = (4 + v)/2$. Possible polyhedra of this type with exclusively quadrilateral, pentagonal, and hexagonal faces and with up to 18 faces are examined. Many of these polyhedra are duals of various triangulated coordination polyhedra studied in previous papers of this series. In order to minimize angular strain, polyhedra with the maximum number of pentagonal faces are favored for water networks in clathrate and semiclathrate hydrates subject to the presence of sufficiently large cavities to accommodate the guest molecule.

In dieser Arbeit werden mögliche konvexe Polyeder für dreidimensionale Wasser-Netzwerke in Klathrat- und Semiklathrathydraten diskutiert. Daher muß die Anzahl der Scheitelpunkte (v), Kanten (e) und Flächen (f) den Gleichungen $e = 3v/2$ und $f = (4 + v)/2$ genügen. Es werden mögliche Polyeder dieses Typs mit bis zu 18 Flächen, die ausschließlich quadrilateral, pentagonal und hexagonal sein sollen, untersucht. Viele dieser Polyeder sind Zwillinge von verschiedenen, aus Dreiecken zusammengesetzten Koordinationspolyedern, die in früheren Arbeiten dieser Reihe untersucht wurden. Um die Winkeldeformation auf ein Mindestmaß zurückzuführen, werden im Falle von Wasser-Netzwerken in Klathrat- und Semiklathrathydraten Polyeder mit der maximalen Anzahl von pentagonalen Flächen bevorzugt, weil so ausreichend große Hohlräume zur Aufnahme des Gastmoleküls entstehen.

Introduction

In recent years the structural chemistry of a novel class of organic hydrates, the clathrate hydrates [2, 3], has received considerable attention. These clathrate hydrates contain a relatively large number of water molecules for each guest molecule. The water molecules in these clathrate hydrates are joined by hydrogen bonding into networks of fused polyhedra. In cases where the guest molecule is an amine, one or more nitrogen atoms of the guest molecule may also be bonded to the fused polyhedral network of water molecules resulting in "semiclathrates" rather than true clathrates [2, 3]. Some of the observed polyhedra [2] in the clathrate and semiclathrate hydrates are rather peculiar ones not otherwise encountered in chemical systems. This paper examines the generation of the polyhedra observed in clathrate and semiclathrate hydrates by appropriate modifications of the techniques successfully used in earlier papers for the study of coordina-

tion polyhedra [4, 5], metal clusters [1], and polyhedral cage boron hydrides [1]. In the polyhedra of the clathrate and semiclathrate hydrates the vertices correspond to tetrahedral or nearly tetrahedral oxygen atoms and the edges to hydrogen bonds between pairs of oxygen atoms.

Generation of Possible Polyhedra

The problem of the generation and evaluation of possible polyhedra for water networks in clathrates and semiclathrates is a more complex problem than the generation and evaluation of possible coordination polyhedra [4, 5], metal cluster polyhedra [1], or boron hydride polyhedra [1] for the following three reasons:

1. There is no inherent direct limitation on the size¹ of polyhedra in clathrate and semiclathrate water networks as in the case of coordination polyhedra where both steric considerations and the number of available orbitals on the central atom impose strict limits on the coordination number and hence on the number of vertices and the size¹ of possible coordination polyhedra [4–6]. Closed metal cluster [1] and boron hydride polyhedra also have an inherent size¹ limitation based on the presence of only triangular faces for maximization of bond delocalization [1] combined with limitations on the maximum vertex order imposed by restrictions on the number of available metal or boron orbitals. A specific example of an extremely large polyhedron found in a clathrate is the irregular 116, 174, 60-polyhedron found² [7] in $[(n-C_4H_9)_3S]F \cdot 23 H_2O$. This polyhedron has 2 quadrilateral faces, 48 pentagonal faces, and 10 hexagonal faces. However, this polyhedron has reentrant edges and hence is not a convex polyhedron but instead a concave polyhedron.

2. The polyhedra in clathrate and semiclathrate water networks are not discrete but instead are joined in an infinite three-dimensional lattice. The space filling properties of convex polyhedra [8] in such infinite three-dimensional lattices indirectly limit the size¹ of polyhedra in water networks. A large convex polyhedron (i.e. one with large v , e , and f values) can be approximated by a sphere. Packing spheres into a three dimensional network always leaves relatively small spaces which correspond to small polyhedra with considerable angular strain. Thus, if only convex polyhedra are considered for the three-dimensional polyhedral network, the size and shape of the relatively small polyhedra necessary to fill the gaps in packing large polyhedra will introduce increasing amounts of angular strain as the size of the large polyhedra increases. A similar limitation on the maximum size of concave polyhedra with one or more reentrant edges does not obtain. However, concave polyhedra may be regarded as derived from the fusion of two or more smaller convex polyhedra such that the volumes of the convex polyhedra overlap. The portions of the convex polyhedra inside the resulting concave polyhedron (i.e. those which bound the region of overlap) are then lost.

¹ As used here the "size" of a polyhedron refers to its volume relative to its edge length. In general a polyhedron with a larger "size" has a larger number of vertices, edges, and faces.

² This notation indicates the number of vertices, edges, and faces, respectively, in various polyhedra as introduced in Ref. [4]. The notation used to indicate the number of faces with various numbers of sides is described by Wells, A.F.: *The third dimension in chemistry*, London: Oxford University Press 1962, and is also used in Table III of Ref. [2].

3. In the semiclathrate hydrates of the alkylamines, the nitrogen atoms of the alkylamine guest molecules form hydrogen bonds with the oxygen atoms of the network of fused water polyhedra. However, since each polyhedron contains only one alkylamine molecule, since the alkylamines forming semiclathrate hydrates contain only one nitrogen atom, and since the polyhedra large enough to enclose the alkylamine guest molecule contain at least twelve vertices, this effect can involve no more than about 10% of the vertices of the water network polyhedra. The perturbations introduced by hydrogen bonding of the nitrogen atoms of the alkylamine guest molecules to the polyhedral water network are small relative to those introduced by the packing properties of polyhedra and therefore may be neglected in this treatment as long as the alkylamine guest molecules contain no more than one nitrogen atom. However, in hexamethylenetetramine hexahydrate [9] where the amine contains four nitrogen atoms, of which three participate in hydrogen bonding, the hydrogen bonding of the hexamethylenetetramine to the water network is significant enough to destroy the basic polyhedral structure, although a regular network is still maintained. The treatment in this paper, therefore, is limited to clathrate hydrates and semiclathrate hydrates where the guest molecule (an alkylamine in all of the known cases) contains no more than one atom which forms hydrogen bonds with the water network. For the reasons stated above such semiclathrate hydrates can be treated as if they were true clathrate hydrates ignoring the single hydrogen bonding interaction between each guest molecule and the polyhedral three-dimensional water network.

For the first two reasons discussed above consideration of possible polyhedra for water networks in clathrates and semiclathrates can be limited to convex polyhedra and restricted to polyhedra with no more than a given number of faces. Such a restriction is also necessary to keep the scope of the problem within manageable limits. The maximum number of faces of polyhedra considered in this work is 18, since this is sufficient to include all known convex polyhedra found water networks in clathrates. The only larger polyhedra found in such water networks are the 26-hedron [10] in $4(\text{CH}_3)_3\text{N} \cdot 41 \text{H}_2\text{O}$ and the irregular 116, 174, 60-polyhedron² [7] found in $[(n-\text{C}_4\text{H}_9)_3\text{S}] \text{F} \cdot 23 \text{H}_2\text{O}$. Both of these large polyhedra are concave with the 26-hedron being formed by fusion of two 14-hedra ($5^{12}6^2$) sharing a common hexagonal face.

The tetrahedral hybridization of the oxygen atoms in hydrogen-bonded water molecules imposes the following basic conditions that all polyhedra for water networks in clathrates must satisfy:

1. *All vertices of the polyhedron must have an order of exactly three.* Each oxygen atom in these water networks has exactly four hydrogen atoms bonded to it. However, only three of the hydrogen bonds attached to any oxygen atom are so directed (i.e. on the same side of a supporting plane (Stutzeben) [11] through the oxygen atom) that they can be edges of the same polyhedron. This indicates a maximum order of three for vertices of polyhedra for water networks in clathrates. Furthermore, geometrical considerations require that each vertex in any three-dimensional polyhedron has an order of at least three. For these reasons, all vertices of polyhedra for water networks in clathrates must have an order of exactly three.

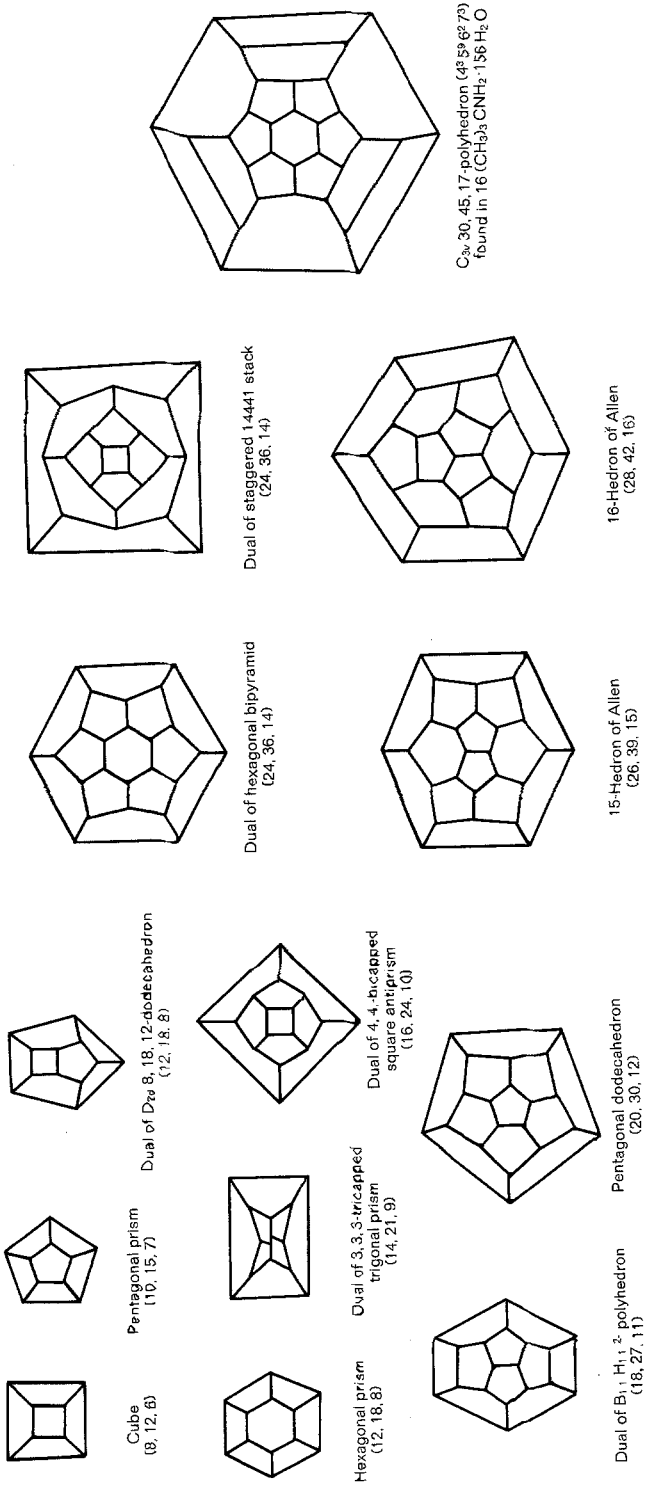


Fig. 1. Schlegel diagrams of some of the polyhedra listed on Table 1

2. *No face of the polyhedron can be triangular and pentagonal faces are greatly favored.* The bond angle for an unstrained tetrahedral atom is $109^{\circ}28'$. This is closest to the 108° interior angle in a regular pentagon. An equilateral triangle has an interior angle of only 60° which is so far from the tetrahedral angle that excessive angular strain prevents the occurrence of triangular faces in polyhedra for water networks. Quadrilateral and hexagonal faces with interior angles of 90° and 120° , respectively, for these polygons when regular have a much smaller and more tolerable amount of angular strain. Furthermore, in the hexagon (as well as in polygons with larger number of sides) possible nonplanarity of the faces provides possibilities for relief of some of the angular strain. Angular strain considerations suggest that the relative tendency for various types of polygonal faces to occur in polyhedra for water networks in clathrates decreases in the following sequence:

Pentagon (most favorable) > hexagon > quadrilateral \gg triangle (least favorable).

In the actual polyhedra many of the faces will not be regular polygons and the angles will not correspond exactly to the $[(n-2)/n] 180^{\circ}$ values required for a regular polygon with n sides. However, the sum of the interior angles of even an irregular (but still planar) polygon with n sides must be a constant $(n-2) 180^{\circ}$. Therefore, as long as planarity is preserved, deviations in one interior angle of a polygon because of irregularity will be compensated by opposite deviations in the other angles. Thus, the angular strain is not appreciably changed by moderate deviations from regularity. Extreme deviations from regularity can only increase the angular strain.

A further complication is that faces of polyhedra with five or more edges need not be planar. Bending of a face can serve to reduce the angular strain in faces with six or more edges. However, bent faces cannot be a major factor in the construction of convex polyhedra for three-dimensional water networks in clathrate hydrates for the following reasons:

1. Incorporation of an outwardly bent face (i.e. one bent in a direction to increase the area enclosed by the polyhedron) introduces reentrant angles into the polyhedron thereby making it concave. Such concave polyhedra may be decomposed into two or more smaller convex polyhedra with overlapping volumes as discussed above. As the concavity of the large concave polyhedron increases, the volume of the convex polyhedra into which the concave polyhedron can be decomposed relative to the volume of the original concave polyhedron decreases and the degree of overlap of the convex polyhedra into which the concave polyhedron can be decomposed decreases. Concave polyhedra can be excluded from consideration in this paper since all concave polyhedra can be decomposed into two or more convex polyhedra of types included in the treatment of this paper.

2. Incorporation of an inwardly bent face (i.e. one bent in a direction to decrease the area enclosed by the polyhedron) will decrease the ability for a given polyhedron to enclose a guest molecule. Hence, inwardly bent faces will only occur when necessary for the polyhedron to remain closed.

These considerations suggest that simple angular strain as discussed above is the major factor in determining the polygons to be found as faces of polyhedra

Table 1. Some possible polyhedra for water networks in clathrates

No. of elements ^a		Name of Polyhedron (if any)	Types of faces ^a			Point group ^b	Examples of clathrates containing this polyhedron
<i>v</i>	<i>e</i>		$f_4 (= q)$	f_5	f_6		
8	12	Cube	6	0	0	O_h	
10	15	Pentagonal prism	5	2	0	D_{5h}	
10	15		6	0	1		
12	18	Dual of D_{2d} -8,18,12-dodecahedron	4	4	0	D_{2d}	16 $Me_3CNH_2 \cdot 156 H_2O$ (empty)
12	18		5	2	1		
12	18	Hexagonal prism	6	0	2	D_{6h}	10 $Me_2CHNH_2 \cdot 80 H_2O$ (empty)
14	21	Dual of 3,3,3-tricapped trigonal prism	3	6	0	D_{3h}	
14	21		4	4	1		
14	21	Dual of 252 stack ^c	5	2	2	C_{2v}	
14	21		6	0	3		
16	24	Dual of 4,4-bicapped square antiprism	2	8	0	D_{4d}	
16	24	Dual of staggered 136 stack ^c	3	6	1	C_{3v}	
16	24	Dual of 262 stack	4	4	2	D_{2h}	
16	24	Dual of staggered 343 stack ^c	5	2	3	C_{2v}	
16	24		6	0	4		
18	27	Existence questionable	1	10	0		
18	27	Dual of $B_{11}H_{11}^{2-}$ polyhedron	2	8	1	C_{2v}	16 $PrNH_2 \cdot 104 H_2O$ (empty)
18	27		3	6	2		
18	27	Dual of 1622 stack ^c	4	4	3	C_{2v}	
18	27		5	2	4		
18	27		6	0	5	C_{2v}	
20	30	Dual of staggered 353 stack ^c	0	12	0	I_h	4 $Me_3N \cdot 41 H_2O$ and many others
20	30	Pentagonal dodecahedron	1	10	1		
20	30		2	8	2		
20	30	Dual of staggered 363 stack ^c	3	6	3	D_{3h}	
20	30	Dual of 22422 stack ^c	4	4	4	D_{2h}	
20	30		5	2	5		
20	30		6	0	6		
22	33		0	12	1		
22	33		1	10	2		
22	33		2	8	3		
22	33		3	6	4		
22	33		4	4	5		
22	33		5	2	6		
22	33	Dual of 16222 stack ^c	6	0	7	C_{2v}	16 $PrNH_2 \cdot 104 H_2O$
24	36	Dual of hexagonal bipyramid ^d	0	12	2	D_{6d}	
24	36		1	10	3		

24	36	14	Dual of staggered 14441 stack ^c	2	8	4	D_{4h}	10 Me ₂ CHNH ₂ · 80 H ₂ O
24	36	14		3	6	5		
24	36	14		4	4	6		
24	36	14	Dual of 22622 stack	5	2	7	D_{2h} D_{3h}	4 Me ₃ N · 41 H ₂ O
24	36	14		6	0	8		
26	39	15		0	12	3		
26	39	15	15-Hedron of Allen ^e	1	10	4	D_{3h} T_d	10 Me ₂ CHNH ₂ · 80 H ₂ O
26	39	15		2	8	5		
26	39	15		3	6	6		
26	39	15	Dual of omnistaggered 33333 stack ^e	4	4	7	D_{2h}	12 Et ₂ NH · 104 H ₂ O
26	39	15		5	2	8		
26	39	15		6	0	9		
28	42	16	16-Hedron of Allen ^e	0	12	4	D_{5h}	
28	42	16		1	10	5		
28	42	16		2	8	6		
28	42	16	Dual of staggered 14641 stack ^e	3	6	7	D_{3d}	
28	42	16		4	4	8		
28	42	16		5	2	9		
28	42	16	Dual of staggered 15551 stack ^e	6	0	10		
30	45	17		0	12	5		
30	45	17		1	10	6		
30	45	17	Dual of omnistaggered 3663 stack ^e	2	8	7		
30	45	17		3	6	8		
30	45	17		4	4	9		
30	45	17	Dual of omnistaggered 3663 stack ^e	5	2	10		
30	45	17		6	0	11		
32	48	18		0	12	6		
32	48	18	Dual of omnistaggered 3663 stack ^e	1	10	7		
32	48	18		2	8	8		
32	48	18		3	6	9		
32	48	18	Dual of omnistaggered 3663 stack ^e	4	4	10		
32	48	18		5	2	11		
32	48	18		6	0	12		

^a For an explanation of these symbols and nomenclature see the text and King, R. B.: J. Amer. chem. Soc. **91**, 7211 (1969).

^b The point groups listed here represent the maximum possible symmetry. In actual cases this may be lowered in a three-dimensional network by various distortions.

^c For an explanation of the "stack" nomenclature see King, R. B.: J. Amer. chem. Soc. **92**, 6460 (1970).

^d For a diagram of the B₁₁H₁₁²⁻ polyhedron see Fig. 5 of Klanberg, F., Muetterties, E. L.: Inorg. Chem. **5**, 1955 (1966).

^e For a description of these polyhedra see Allen, K. W.: J. chem. Physics **41**, 840 (1964).

^f This polyhedron is the 14-hedron of Allen (see footnote e).

in three-dimensional water networks and that relief of strain by bending will not cause polygons with more sides than those favored by angular strain considerations to become predominant as faces in the construction of such polyhedra.

The first paper of this series [4] listed relationships between the parameters describing closed convex three-dimensional polyhedra with only triangular and quadrilateral faces. The following are the analogous relationships between the parameters describing closed convex-dimensional polyhedra with all vertices of order three:

1. Euler's Relationship [12]: $e + 2 = v + f$.
2. Relationship between the Edges and Vertices: $3v = 2e$.
3. Relationship between the Edges and Faces: $\sum_i if_i = 2e$. Here f_i refers to the

numbers of faces with i sides or edges. Thus f_4 refers to the number of quadrilateral faces (designated as q in the first paper of this series [4]).

4. Totality of Faces: $\sum_i f_i = f$.

For any closed convex three-dimensional polyhedron with all vertices of order three the numbers of edges and faces for a given number of vertices are uniquely defined by the relationships $e = 3v/2$ and $f = (4 + v)/2$. This reduces drastically the number of sets of v , e , and f values which have to be considered. For a given set of v , e , and f values there are many possible polyhedra corresponding to different solutions of the equations $\sum_i if_i = 2e$ and $\sum_i f_i = f$.

Table 1 summarizes the possible closed convex three-dimensional polyhedra with all vertices of order three, with no more than eighteen faces, and with only quadrilateral, pentagonal, and hexagonal faces. Figure 1 shows Schlegel diagrams [12] of some of the more important of these polyhedra in the chemistry of clathrate water networks.

Identification of the actual polyhedra corresponding to various sets of v , e , f , and f_n values is relatively difficult in many cases but has been achieved for the polyhedra of greatest potential importance in polyhedral water networks in clathrates. The relationship of duality [13], briefly cited in the first paper of this series [4], is of considerable value in the identification of the polyhedra listed in Table 1. In a pair of (mutually) dual polyhedra P_a and P_b the vertices of one of the polyhedra correspond to the faces of the other and vice versa. Both P_a and P_b belong to the same symmetry point group. Furthermore, the following relationships are satisfied where the subscripts a and b refer to the dual polyhedra P_a and P_b , respectively: $v_b = f_a$; $e_b = e_a$; $f_b = v_a$. The correspondence of a vertex of a polyhedron P_a to a face of a polyhedron P_b and vice versa also mean that the following relationships must be satisfied for all n : $(j_n)_a = (f_n)_b$ and $(f_n)_a = (j_n)_b$. One obvious consequence of the latter set of relationships is that the polyhedra with all vertices of order three generated in Table 1 all are duals of some triangulated polyhedron [4]. Triangulated polyhedra are of interest as coordination polyhedra [4, 5], metal cluster polyhedra [1], and cage boron hydride polyhedra [1] and thus were discussed in earlier papers of this series. Many of the polyhedra in Table 1 can be identified as duals of previously observed triangulated polyhedra. The "parallel plane method" for generating polyhedra [5] is useful for generating duals of polyhedra in Table 1. The existence of the 18, 27, 11-polyhedron (4^15^{10})

is regarded as unlikely (although not yet rigorously disproved) since all previous attempts during the study on polyhedra for high coordination numbers [5] to find its dual (i.e. an 11, 27, 18-polyhedron with no vertices of order six or higher) were unsuccessful.

Discussion

The pentagonal dodecahedron is the optimum polyhedron for water networks in clathrates and semiclathrates since it is the only polyhedron with all vertices of order three where all faces are the favored pentagons with minimum angular strain. The pentagonal dodecahedron cannot be packed into a lattice if it is kept regular with idealized I_h symmetry [14]. However, if the pentagonal 108° angles in the pentagonal dodecahedron are distorted slightly to the tetrahedral value of $109^\circ 28'$, then pentagonal dodecahedra can form a network with cubic symmetry. This network also contains larger 28, 42, 16-polyhedral ($5^{12}6^4$) holes which represent a distorted C_{2v} version of the idealized T_d polyhedron of this type. In another packing of pentagonal dodecahedra larger holes are also generated which correspond to the 24, 36, 14-polyhedron ($5^{12}6^2$), i.e., the dual of the hexagonal bipyramid, and to the 26, 39, 15-polyhedron ($5^{12}6^3$). These water networks with pentagonal dodecahedra are found in numerous clathrate hydrates and gas hydrates [2, 3]. The water networks containing pentagonal dodecahedra may also contain the 14-hedra, 15-hedra, and 16-hedra with the maximum numbers of the favored pentagonal faces.

A pentagonal dodecahedron in a water network has a volume of about 170 \AA^3 [15]. Some types of guest molecules in a clathrate or semiclathrate hydrate will be either too large or of the wrong shape to fit into a cavity of this size and shape. In some cases the guest molecules can be accommodated in the somewhat larger 24, 36, 14-polyhedra ($5^{12}6^2$) (volume $\sim 220 \text{ \AA}^3$) or 26, 39, 15-polyhedra ($5^{12}6^3$) (volume $\sim 240 \text{ \AA}^3$) which form the larger cavities in one of the packings of pentagonal dodecahedra. The still larger 28, 42, 16-polyhedron ($5^{12}6^4$) is found in isopropylamine hydrate $10(\text{CH}_3)_2\text{CHNH}_2 \cdot 80 \text{ H}_2\text{O}$ [16].

Clathrate and semiclathrate hydrates of relatively bulky amines contain still larger polyhedra. Thus, the water network of diethylamine hydrate, $12(\text{C}_2\text{H}_5)_2\text{NH} \cdot 104 \text{ H}_2\text{O}$, contains D_{3d} 32, 48, 18-polyhedra ($5^{12}6^6$); the diethylamine molecules fit relatively well into these ellipsoidal cavities [17]. This network of 32, 48, 18-polyhedra ($5^{12}6^6$) contains no pentagonal dodecahedral cavities but instead some irregular concave 29, 44, 17-polyhedra ($4^35^86^6$) which because of their concavity contain one vertex of order four. The water network of t-butylamine hydrate, $16(\text{CH}_3)_3\text{CNH}_2 \cdot 156 \text{ H}_2\text{O}$, the only known amine clathrate hydrate without hydrogen bonding of the amine to the water network, contains unusual C_{3v} 30, 45, 17-polyhedra ($4^35^96^27^3$); [18] this is the only polyhedron with heptagonal faces encountered in clathrate hydrates (polyhedra with heptagonal faces have been omitted from Table 1, since consideration of such polyhedra increases the possibilities to an unmanageable number). Packing these 30, 45, 17-polyhedra ($4^35^96^27^3$) into a three-dimensional network leaves small cavities of 12, 18, 8-polyhedra (4^45^4); this polyhedron is the dual of the D_{2d} 8, 18, 12-dodecahedron which is the most common coordination polyhedron for eight-coordinate

complexes [4, 19]. The 12, 18, 8-polyhedra (4^45^4) in $16(\text{CH}_3)_3\text{CNH}_2 \cdot 156 \text{H}_2\text{O}$ are far too small to accommodate any guest molecules. However, the 30, 45, 17-polyhedron ($4^35^96^27^3$) has a free volume about 30% larger than that of the 28, 42, 16-polyhedron ($5^{12}6^4$); this additional volume may be necessary to accommodate the relatively bulky t-butylamine molecule. Furthermore, the failure of the t-butylamine in its clathrate hydrate to form hydrogen bonds with the polyhedral water network may make a larger polyhedron necessary to enclose it in to keep the t-butylamine molecules beyond the bonding distances to the atoms in the water network. Most of the faces of both the 32, 48, 18-polyhedra ($5^{12}6^6$) and the 30, 45, 17-polyhedra ($4^35^96^27^3$) are the favored pentagons.

The theory developed in this paper suggests that the normal water network for clathrates and semiclathrates contains the very favorable pentagonal dodecahedron. However, if the guest molecules are too large to fit into the cavities of pentagonal dodecahedra (e.g. diethylamine and t-butylamine), then alternative water networks with larger polyhedra will be formed. This suggests that clathrate and semiclathrate hydrates of relatively large and non-spherical molecules which do not fit into the polyhedra with up to 18 faces discussed in this paper are most likely to contain unusual polyhedra. However, a limiting factor in the preparation of clathrate hydrates of large molecules of appropriate polarity is likely to be the difficulty of packing large convex polyhedra into a three-dimensional network because of the concurrent need in such networks for strained small polyhedra both to fill the gaps between the large polyhedra and to accommodate the fourth hydrogen bond to each oxygen atom.

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Prof. Dr. R. B. King
Department of Chemistry
University of Georgia
Athens, Georgia 30601, USA