

Clathrates – An Exploration of the Chemistry of Caged Compounds

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Clathrate are host-guest complexes. They are discussed with specific examples from different branches of chemistry. Clathrates are formed in different environments, but ultimately yield cage type of structures. Depending on the type of host-guest molecules, clathrates of different dimensions and properties are formed.

Introduction

Clathrates are 'caged' or 'enclosed' compounds. The word clathrates is derived from the latin word 'clathratus' meaning enclosed or protected by cross bars of a grating. In such compounds one of the components has an open structure in the crystalline state containing cavities, holes or channels in which atoms or molecules of another component with appropriate size are trapped. The trapped molecule is called the 'guest' while the other is the 'host'. So, clathrates are host-guest complexes. Such complexation can occur both in solution and in the solid state. In solid state, guests are retained by the host through crystal lattice forces. In each case there is complete enclosure of the molecules of the guest in suitable cage structure formed by the molecules of the host. Such caged host-guest complexes are variously referred to as supramolecular assembly, extramolecular assembly, inclusion compounds, occlusion compounds and clathrates.

The guest atoms or molecules can be encapsulated into host cages if their size is comparable to the size of the available empty space within the cage. The sole determining factor in the formation of clathrates is proper molecular size. Molecules which are too large do not fit into the cage and those which are too small escape through the lattice work. The cage is held together by

Keywords

Clathrates, host-guest complex, cage structure, fullerenes, gas hydrates, clathrin.



very weak forces like hydrogen bonding, ion pairing, dipole-dipole interaction and van der Waals attraction. Analysis indicates that the composition of clathrates is slightly less than the expected stoichiometric ratio of the host to guest molecules. This suggests that all the available cavities may not be used. The reason for this can be understood from the enclosing process. A guest molecule must be properly oriented at the moment of enclosure; if not, it will be excluded and some unfilled holes are to be expected.

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Background

The study of clathrates began as early as 1811, when the first scientific report on a chlorine-ice compound with unidentified nominal composition that had earlier been thought to be crystalline chlorine appeared in the literature. Twelve years later Faraday revised the data and determined its stoichiometry to be $\text{Cl}_2(\text{H}_2\text{O})_{10}$. In 1886, Mylius observed interesting and intriguing features in the complex compounds formed by hydroquinone with certain volatile substances. He suggested that in some way the molecules of one component were able to lock the molecules of the second component into position, but without chemical bonding. Interest in this unusual behaviour was revived by the work of Palin and Powell who, over 60 years later, verified the results of Mylius by means of X-ray studies. Powell in 1948 proposed that the compounds be called clathrate compounds. The correct formula was determined as $\text{Cl}_2(\text{H}_2\text{O})_{5.75}$, and the complex was described as a 3-D network of fused large polyhedra incorporating channels and cages occupied by the 'guest impurities'. In 1965, the first clathrate compounds of silicon with sodium as guest were synthesized. These compounds were $\text{Na}_8\text{Si}_{46}$ and $\text{Na}_x\text{Si}_{136}$ ($x=3-11$). In 1969, the first germanium and tin clathrates, K_8Ge_{46} and K_8Sn_{46} , were synthesized.

Classification

Clathrates are a relatively unexplored class of compounds, their formation is interesting and their properties are unique. They

are a part of every area of chemistry namely, inorganic, organic and biochemistry. Clathrates are formed in different pressure and temperature environments involving different host-guest molecules. Accordingly, clathrates are broadly classified as given below.

- High temperature and high pressure clathrates, e.g., fullerenes.
- Low temperature and high pressure clathrates, e.g., gas hydrates.
- Normal temperature and pressure clathrates, e.g., clathrin.
- Moderately high temperature and low pressure clathrates, e.g., zeolites.

Fullerenes

Fullerenes, the novel carbon allotropes, are clathrates of carbon cages that encapsulate atomic or molecular species. The hollow cage structure are made up of hexagonal and pentagonal homoatomic shells of carbon. Twenty hexagons and twelve isolated pentagons interact to form one C_{60} , a truncated icosahedron which is made up of 60 carbon atoms bonded by 30 double bonds and 60 single bonds. A truncated icosahedron is represented by a football-like structure (*Figure 1a*). Fullerenes have a general formula C_{20+2n} , where $n=0,2,3,4, \dots$ and $n \neq 1$. Commonly available fullerenes are C_{20} , C_{32} , C_{60} , C_{70} , C_{80} , C_{540} .

Fullerene- C_{60} has an inner diameter of 7.1 Å which is large enough to enclose the noble gases like He, Ne, Ar, Kr and Xe. Noble gases of a specific isotopic composition can be introduced during the synthesis of fullerenes at high temperature and pressure. The encapsulated gases are the guests and the fullerenes are the host and they together form the host-guest complex. Fullerene with one or more guest molecules encapsulated into its cage is termed as endohedral fullerene (*Figure 1b*). Even metals like Scandium (Sc), Yttrium (Y), Holmium (Ho), Gadolinium (Gd), Uranium (U), Neptunium (Np) and Americium

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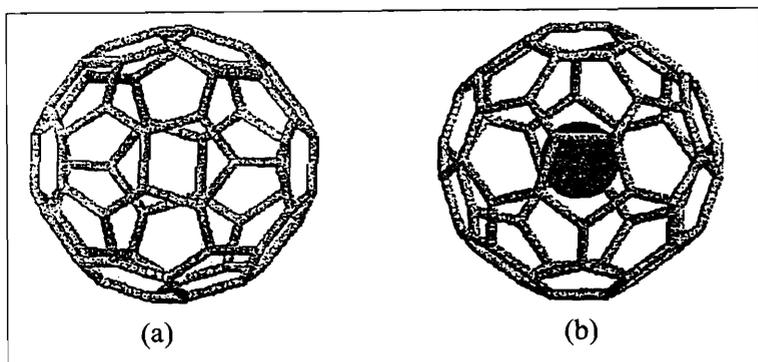


Figure 1. (a) Fullerene (b) Fullerene with a guest atom inside – endohedral fullerene.

(Am) can be encapsulated into fullerene cages. When a metal is encapsulated it is termed as metallo-fullerene. Fullerenes can encage more than one atomic species as guest. For example in $M_3N@C_{80}$ fullerene, three metallic atoms and one nitrogen atom are engaged in one C_{80} . (M is a metal and @ indicates encapsulated or endohedralised.)

Fullerenes are found deep inside the earth close to the core and also at meteoritic impact locations, where high temperature and pressure conditions exist.

Encapsulated (endohedral) fullerenes have captivated scientists with their properties and possibilities for application. They serve as non-dissociating salts in electrochemistry, for example, with a negatively charged cage encapsulating a positively charged ion. They also offer exciting electronic and magnetic properties and might find uses in quantum computing or biomedical applications.

The ability of fullerenes to encage one or more metallic atoms inside the cage helps as contrast-enhancing agents for Magnetic Resonance Imaging (MRI). Contrast agents enhance the quality of MRI images, aiding in the detection and diagnosis of injuries or abnormal growth in the human body. Gadolinium(III) chelates serve as the leading commercial MRI contrast agents. When Gd^{3+} locked up in organic chelates is injected into the body it can magnetically tickle water protons present in tissues leading to higher signal intensity and greater contrast in the

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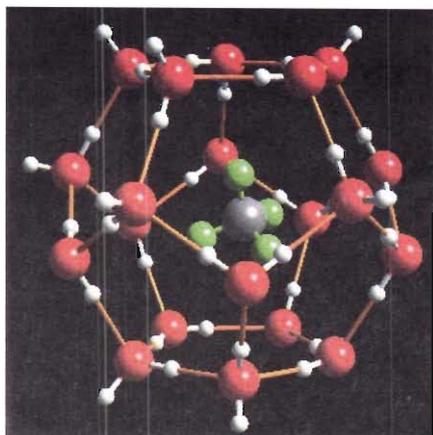


Figure 2. Structure of gas hydrate. [1]

Credit: University of California, Lawrence Livermore National Laboratory and Department of Energy, USA.

MRI images. But, at times this toxic heavy metal (Gd) may react with bio molecules as the chelate winds its way through the body. But, encapsulating the Gd inside a fullerene is safer and such endohedral fullerenes offer additional advantages in the medical field.

Gas Hydrates

Gas Hydrates, also called water clathrates, are the naturally occurring solids of water and natural gas. The water molecules form a rigid lattice of cages enclosing molecules of natural gas, mainly methane(CH_4). Water

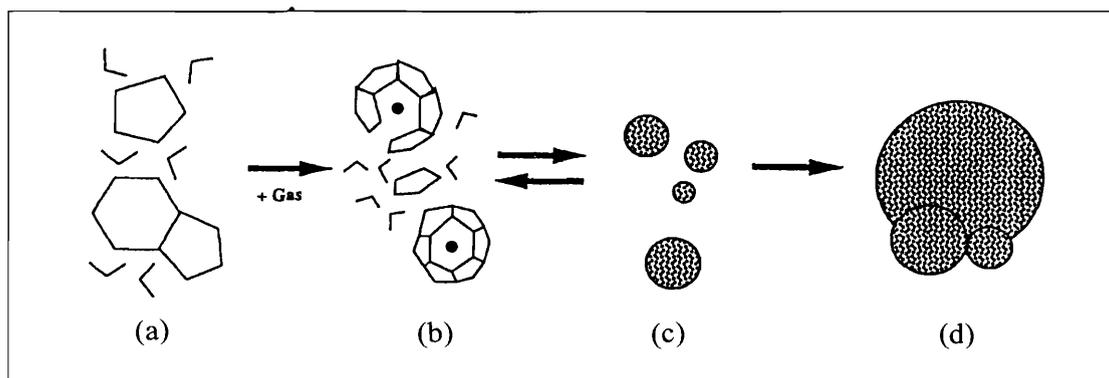
crystallizes in the isometric crystallographic system (cubic lattice structure) rather than the hexagonal system of normal ice. The gases enclosed may be Ar, Kr, Xe, Cl_2 , H_2S , N_2 , O_2 and hydrocarbons like methane, ethane, and propane. The structure of methane gas hydrate is shown in *Figure 2*.

Gas hydrates are generally formed at low temperatures and high pressures. Because of these conditions their formation in nature is restricted to two geological settings, the polar regions of the continental part, the shelf and the deep oceanic part. They are also found on the icy moons of our solar system, at Saturn and beyond. Deep inside the oceans, due to lower temperature, water begins to solidify. The oceans are rich in hydrocarbons due to the presence of dead plants and animals. The decay and decomposition of these organisms releases methane and other gases that may get entrapped in the solidifying water to form gas hydrates.

A hypothetical mechanism for the kinetics of hydrate formation as proposed by Long and Sloan is as follows (*Figure 3*). Pure water exists with ring structures of pentamers and hexamers as shown in *Figure 3a*. Gas molecules get entrapped in water when water solidifies forming gas hydrate molecules as shown in *Figure 3b*. These clusters combine leading to agglomeration (*Figure 3c*). Finally, when the size of the cluster agglomerates reaches a critical value, growth begins (*Figure 3d*). Gas hydrates

Gas molecules get entrapped in water when water solidifies forming gas hydrate molecules.





are potential source of future energy requirement as they store a large quantity of natural gas.

India is collaborating with Russia for exploration of gas hydrates in Indian ocean area. Gas hydrates are metastable. Destabilised gas hydrates beneath the seafloor can enhance global warming and cause climatic changes. The decomposition and blow out of gas from gas hydrates explain the mystery of the Bermuda triangle, located in the Atlantic ocean to the east coast of USA.

Clathrin

Clathrates play an important role in biological processes as well. The specificity and efficiency of biological processes can be attributed to the efficient organization of biological media. Clathrin, a protein, plays a major role in membrane bound transport package, and is a clathrate-like host-guest system.

The clathrin protein is known to take the shape of a triskelion, with three bent legs, as shown in *Figure 4a*. Each leg is made up of seven repeating units and each unit is made up of ten helical structures. The triskelions are arranged in a lattice-like network of hexagons and pentagons as shown in *Figure 4b*. Triskelions self-assemble into hollow structures (cages) due to the interactions between proximal and distal legs that hold the lattice together. This cage structure is similar to the host in clathrate compounds. Lipids and proteins (cargo) are engulfed into this clathrin-coated vesicle as illustrated in *Figure 4c*. The clathrin

Figure 3. Mechanism for kinetics of gas hydrate.

Credit: E Dendy Sloan

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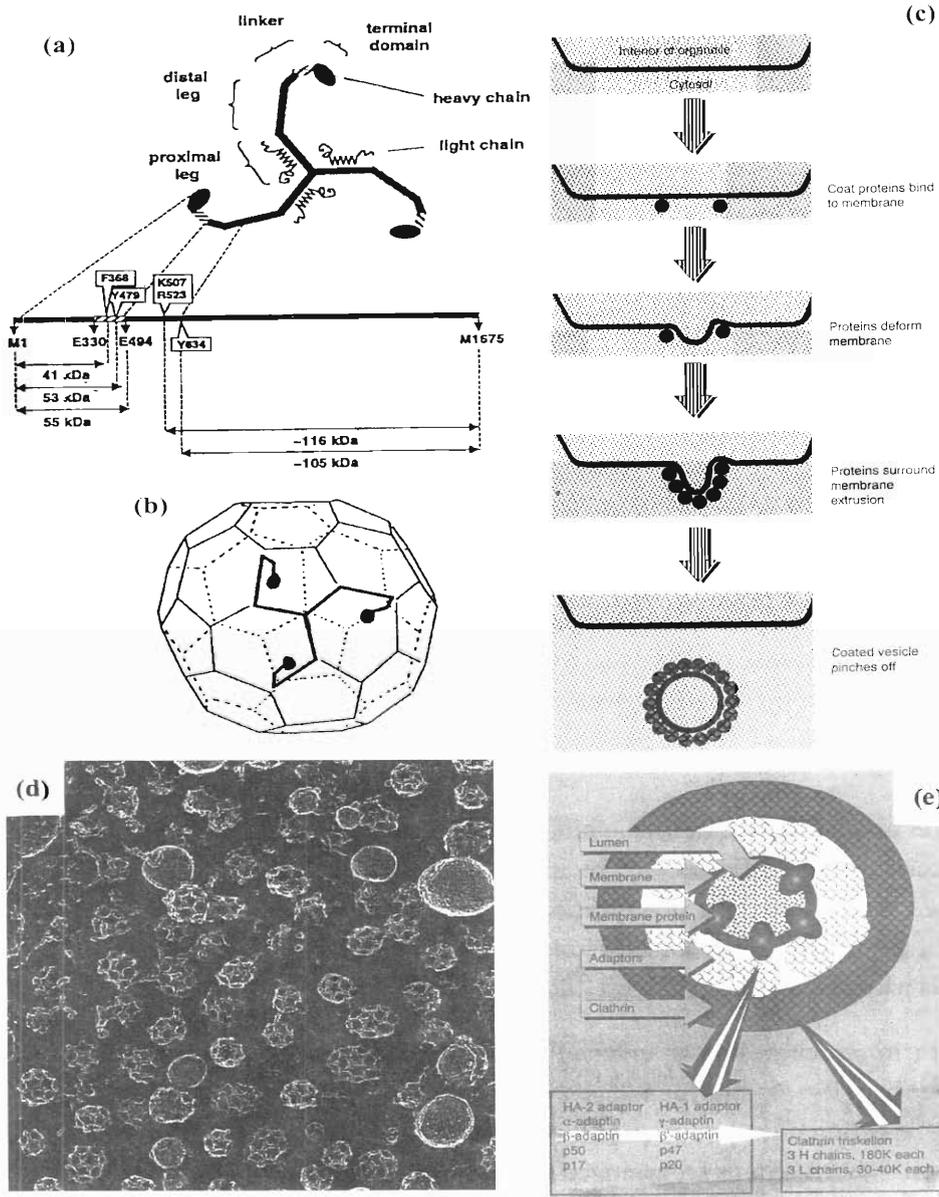


Figure 4. Clathrin structure (a) Triskelion with three bent legs. (b) Triskelions self-assemble forming cages. (c) Endocytic pathway using clathrin coated vesicle. (d) Polyhedral lattice on clathrin surface (e) Cross-section of clathrin coated vesicle.

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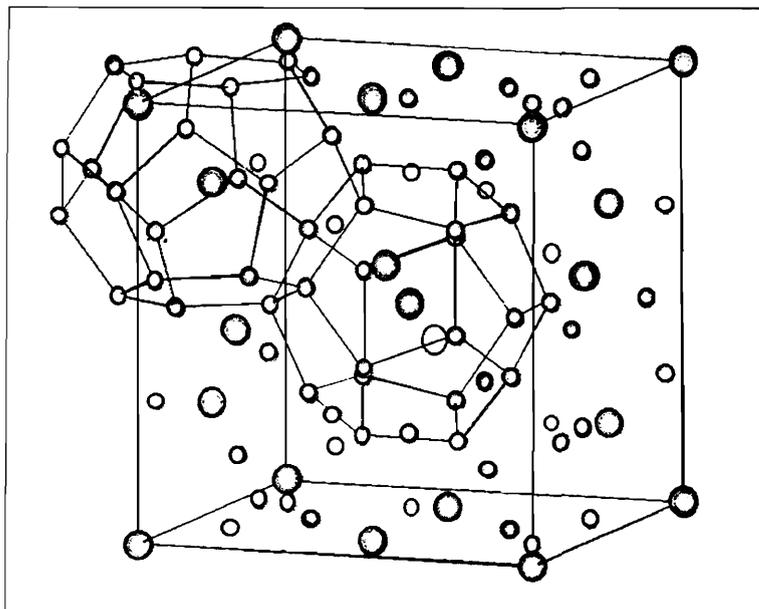


Figure 5. Inorganic clathrates. The small circles indicate host atoms (Si, Ge or Sn) which form a 3-D network enclosing larger circles representing the guest atoms (alkali or alkaline earth metals). Two such clathrates are depicted in a cubic cell.

protein binds to the membrane leading to membrane deformation. It surrounds the membrane exclusion and finally the clathrin coated vesicle (host) pinches off with the cargo (guest) engulfed. Vesicles have a polyhedral lattice on the surface, created by triskelions of clathrin as indicated in *Figure 4d*. A cross-section of clathrin coated vesicle is depicted in *Figure 4e*. These vesicles are involved in intracellular transport of cargo between the cell organelles. On reaching the delivery site, uncoating occurs and the cargo is delivered. Clathrin-coated vesicles are the most prominent of the carriers in endocytic pathways.

Inorganic Clathrates

Inorganic clathrates are crystalline solids with 3-D frameworks made up of tetravalent and trivalent atoms which enclose guest atoms. In binary compounds, the framework can be made of Silicon, Germanium or Tin atoms. Si and Ge both crystallize in cubic face centred diamond-type lattice and form a stable and rigid covalent network. The guests are generally alkali and alkaline-earth atoms. The cavity size of Si and Ge are comparable only with those of Na^+ or K^+ and compounds like K_8Ge_{46} ,



The cavity size of Si and Ge are comparable only with those of Na^+ of K^+ and compounds like K_8Ge_{46} , $\text{Na}_8\text{Si}_{46}$, $\text{Na}_x\text{Si}_{136}$ ($X=1-24$) etc. are formed. Rb^+ and Cs^+ are too large to be incorporated into the cages of Si and Ge.

$\text{Na}_8\text{Si}_{46}$, $\text{Na}_x\text{Si}_{136}$ ($X=1-24$) etc. are formed. Rb^+ and Cs^+ are too large to be incorporated into the cages of Si and Ge. Sn, however, forms clathrates with Rb^+ and Cs^+ yielding solids like $\text{Rb}_2\text{Cs}_6\text{Sn}_{46}$, $\text{Cs}_8\text{Sn}_{46}$, $\text{K}_{1.6}\text{Cs}_{6.4}\text{Sn}_{44}$ and others. *Figure 5* shows the inorganic clathrate structure. Inorganic clathrates can be synthesized by carrying out reactions at 650°C and 10^{-5} mm Hg pressure over a period of three weeks to ensure better diffusion of the alkali metals into Si and Ge.

There are results to support the idea that strong charge-transfer interactions exist between Si/Ge and the alkali metal atoms, although the resulting structure cannot be considered entirely ionic. The $\text{Na}_x\text{Si}_{136}$ ($x < 9$) system is speculated to encapsulate neutral alkali metal atoms rather than Na^+ ions, i.e., there is no electron transfer over the Si or Ge network but isolated free alkali metal atoms in the cage. At higher Na concentrations insulator-to-metal transition occurs as Na electrons are delocalized (full occupation of all sites $\text{Na}_{24}\text{Si}_{136}$) due to significant overlap between the Na and Si orbitals.

Clathrates with partial or complete substitution of Si, Ge and Sn by Al, Ba, In, Ga or other transition metals have also been synthesized. $\text{Eu}_8\text{Ga}_{16}\text{Ge}_{30}$, $\text{Cu}_8\text{Ge}_{40}\text{Ba}_6$, $\text{K}_8\text{In}_{18}\text{Si}_{28}$ are such examples. $\text{Eu}_8\text{Ga}_{16}\text{Ge}_{30}$ is a clathrate with guest sites fully occupied by a rare-earth element. Their properties can be varied from semiconducting, metallic to superconducting by encapsulating different metal species inside the cage.

The interest in inorganic clathrates has increased enormously because of the discovery of superconductivity in $\text{Ba}_y\text{Na}_x\text{Si}_{46}$ and $\text{Ba}_8\text{Si}_{46}$. It was unprecedented because no other example of superconductivity was known for phases with covalent sp^3 bonding. When forming they appear to disdain the normal types of bonding and seldom fall into strictly inorganic or organic classifications. Recent research findings showed that the silicon clathrates have low compressibility and therefore are considered potential superhard materials.

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Physical properties such as Seebeck coefficient or thermopower (S), electrical (s) and thermal (l) conductivities of the clathrates can be changed by altering the guest atoms in the host cages and thus serving as potential thermo-electric materials. Si and Ge clathrates are considered promising candidates for thermo-electric applications because of their relatively large unit cells with “voids and rattlers inside them”. They are the important prerequisites for scattering of heat carrying phonons and thereby for low phonon-contributed thermal lattice conductivities.

Zeolites

In inorganic clathrates when a SiO_4 tetrahedron shares all its four oxygens with other SiO_4 tetrahedra, the result is the formation of a 3-D lattice. Isomorphous replacement of Si^{4+} by a combination of Al^{3+} and other metal ions gives minerals known as feldspar, zeolite and ultramarines. Among these compounds zeolites are the most useful ones. The characteristic feature of zeolites is the openness of the structure which permits the formation of channels and cavities of different sizes. Zeolites are described as broad class of micro-porous materials with crystalline walls and unique internal pore system with honey comb structure. Water molecules and a variety of other molecules like NH_3 , CO_2 and $\text{C}_2\text{H}_5\text{OH}$ can be trapped in these channels or cavities. Thus, zeolites act as ion-exchangers and as molecular sieves. This mineral loses water rapidly on heating and seemed to boil. The name ‘zeolite’ comes from the Greek word zeo (to boil) and lithos (stone). The zeolite is represented by the general formula $M_{x/n}\{(\text{AlO}_2)_x(\text{SiO}_2)_y\}.z\text{H}_2\text{O}$, where M = Metal cation like Na^+ , K^+ or Ca^{2+} , n = charge of the metal cation, and z = number of moles of water of hydration.

The position, size and number of cations as well as the position and number of water molecules can significantly alter the properties of the zeolite. Generally, organic and inorganic molecules are introduced into the zeolite cavities as guest.

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Even though the guest and host molecules are different in gas hydrates and inorganic clathrates, they belong to clathrate-I type because of their similar structure and same number of host-guest molecules occupying the lattice.

The inclusion properties of zeolites have found wide industrial applications. Hazardous and toxic fluids found in nature can be absorbed, trapped or neutralized by zeolite. For example they are used for separation and storage of nuclear waste. They can also be used as water softener by exchange of their metal cations.

Types of Clathrate Structures

Inorganic clathrates and hydrates are classified into two categories depending on their structure and number of host-guest molecules. They are referred to as clathrates of type-I and II, and their characteristics are described below.

Clathrates with 46 host and 8 guest atoms are known as type-I clathrates. They are represented by the general formula as G_8B_{46} . there are eight cages per formula unit, two small and six large and therefore written as $G'_2G''_6B'_{46}$, where G' and G'' are different guest molecules; B represents host atoms / molecules and is termed as clathrand. When B is water molecule, type-I clathrates are termed as gas hydrates; the guest (G) can be Ar, Kr, Xe, H_2S , Cl_2 , CH_4 gases and the host (B) is water molecule.

The prototype of clathrate-I structure for gas hydrate has a stoichiometry $G_8(H_2O)_{46}$. The inorganic clathrates can have different combination of host-guest molecules and can be written as $G_8(B)_{46}$, $G'_2G''_6(B)_{46}$, $G_8B_{23}B'_{23}$, $G_8B_8B'_{38}$, $G_8B_{16}B'_{30}$, $G_8B_{18}B'_{28}$. There are seven binary or pseudo-binary compounds between alkali metals and group IV elements with clathrate-I structure. Some of them are Na_8Si_{46} , K_8Ge_{46} , K_8Sn_{46} , Cs_8Sn_{46} . Even though the guest and host molecules are different in gas hydrates and inorganic clathrates, they belong to clathrate-I type because of their similar structure and same number of host-guest molecules occupying the lattice.

All the 46 clathrand atoms of clathrate type-I are tetrahedrally coordinated and their arrangement in the unit cell is such that one can define two polyhedra of different sizes. One is a 20-atom pentagonal dodecahedron (5^{12}) and the other is a 24 atom tetrakaidecahedron ($5^{12} 6^2$). The symbol ($5^{12} 6^2$) indicates a

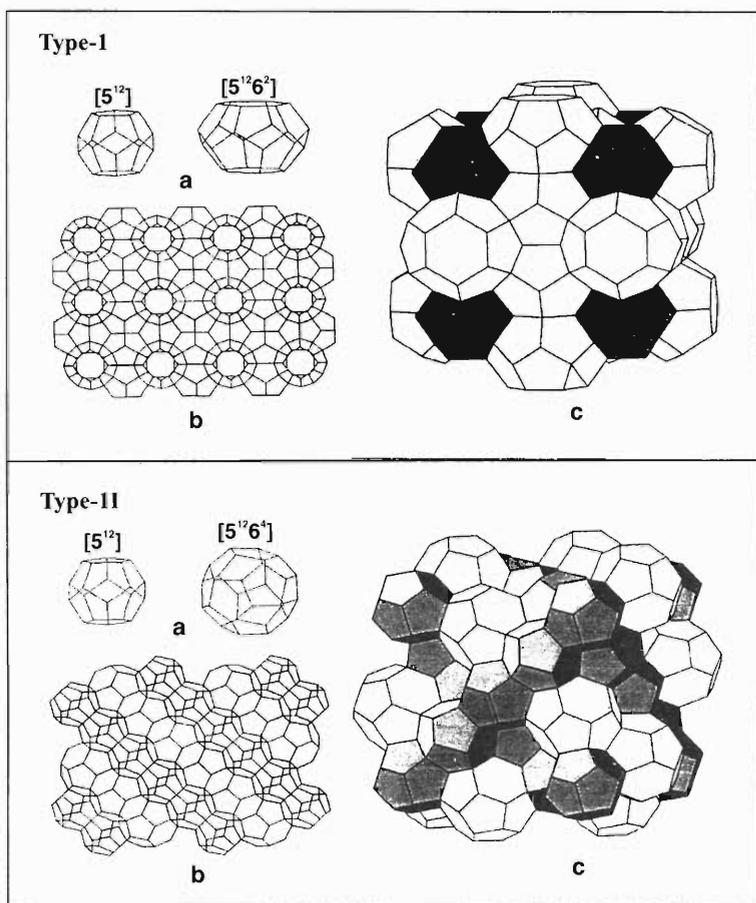


Figure 6. Different types of Clathrate structures.

Type-I structure: (a) Building units of clathrate type-I structure; (b) Clathrate type-I layer; (c) Polyhedral representation of clathrate-I unit cell.

Type-II structure: (a) Building units of clathrate type-II structure; (b) Clathrate type-II layer; (c) Polyhedral representation of clathrate-II unit cell.

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polyhedron with 12 pentagonal and 2 hexagonal faces. The tetrakaidecahedra create a system of three mutually perpendicular 'channels' by sharing common hexagonal faces. Three pairs of channels enclose the smaller dodecahedra and separate them from each other. Clathrate-I phases crystallise in cubic lattices. *Figure 6* shows the structure of type-I clathrate. Type-I gas hydrates are generally formed in deep oceans from biogenic gases.

Clathrates with 136 clathrands and 24 guests are referred to as type-II clathrates. They are represented as $G_{24}B_{136}$ or $G_{16}G'_8B_{136}$ where G is the guest atom and B is the clathrand. In type-II clathrates, G can be H_2S , CO_2 , $CHCl_3$, n-propane, nitromethane or cyclopentane. When B is a water molecule, they are termed as

Type-I gas hydrates are generally formed in deep oceans from biogenic gases.



Clathrate-II hydrates are formed from natural gases or oils. They represent hydrates from thermogenic gases.

liquid hydrates or double hydrates. Clearly the guest atoms/molecules in this case are larger than in type-I clathrates.

The framework-building atoms form nearly ideal tetrahedral environment. Here, in addition to the pentagonal dodecahedron (5^{12}), the second type polyhedra are built of 28 atoms, hexakaidecahedra ($5^{12} 6^2$) that have 12 pentagonal and 4 hexagonal faces. They are linked to each other by their hexagonal faces forming a diamond-like structure within a cubic framework. The smaller pentagonal dodecahedra are not isolated as in the clathrate-I structure but are rather linked through common faces to form layers. The clathrate-II crystallizes in the face-centred cubic. *Figure 6* shows the structure of clathrate-II. Clathrate-II hydrates are formed from natural gases or oils. They represent hydrates from thermogenic gases.

The stoichiometries of the two types of clathrates do not differ much. When normalized, their (completely filled) chemical formulae are $GB_{5.75}$ and $GB_{5.67}$ for clathrates-I and -II respectively. Structurally, however, they are noticeably different. The type-I clathrates are found to be more stable than the type-II. Therefore, out of the 50 phases of inorganic clathrates reported, a vast majority of them are clathrates of type-I structure. The cavity size of type-II clathrates is greater than that of type-I. The size of the stabilising guest molecules ranges between 0.35 and 0.75nm for clathrate-I and II. Guest molecules with sizes greater than 0.75 nm are too large for inclusion in the cavities and less than 0.35nm are too small and escape from the cavity.

Applications

Some of the present applications of clathrates are listed below.

1. Medical applications such as in magnetic resonance imaging.
2. Used to study the photo-behaviour of organic and inorganic molecules by introducing them as probes (guests) into clathrate cages.
3. Resolution of racemic mixtures.

The type-I clathrates are found to be more stable than the type-II.



4. Zeolites can remove atmospheric pollutants, ozone-depleting CFC's and harmful organics from water.
5. Since clathrate compound formation is based on molecular size rather than on chemical similarity, it can be used practically in the separation of chemically similar but physically different molecules. These compounds are now emerging on the chemical scene to take a place of increasing importance.
6. They are used as materials for superconductivity (Ba-Na-Si₄₆ series).

Future prospects:

1. Pharmaceutical preparation by clathration separation appears promising.
2. Clathrates provide a convenient means of storing radioactive isotopes of Kr and Xe produced in nuclear reactors and also toxic fluids found in nature.
3. Useful for studies of air pollution, process control and meteorology.
4. They display intriguing lattice and electronic properties pointing at future potential applications.
5. Potential candidates for thermoelectric applications due to their thermal conductivity. Inorganic clathrates can be used as superhard materials.

Suggested Reading

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