Hexamethylenetetramine Hexahydrate: A New Type of Clathrate Hydrate

Abstract. *Hexamethylenetetramine hexahydrate has a three-dimensional framework structure of hydrogen-bonded water molecules. Each hexamethylenetetramine molecule is located in a cavity within this framework but is linked to the water structure by hydrogen-bonds through three of its four nitrogen atoms.*

The term "clathrate" was first introduced by Powell (*1*) to describe a molecular compound in which guest molecules of one or more species are encaged in a host lattice formed by molecules of another species. The clathration was considered to be physical, in the sense that it does not involve primary chemical bonds (*2*). The well-known compounds formed of hydroquinone and inert gases (*3*) and the gas hydrates (*4*) belong to this class of molecular compound. A variation from this category has been explored through the studies of the crystal structures of certain peralkylated ammonium salt hydrates (*5*). In those structures the anions are hydrogen-bonded within the water host lattice, and the guest species are the cations. The electrostatic interaction between the anionic host lattice and cationic guests is so distributed that the interatomic distances involved are indistinguishable from those associated with the van der Waals interactions between the neutral host and guests in the gas hydrate structures.

In this paper we report the discovery of another variation of the clathrate type of hydrate structure, in hexamethylenetetramine hexahydrate, $(CH_2)_6N_4 \cdot 6H_2O$. By cooling a saturated aqueous solution slowly towards 0°C, this crystalline hydrate is obtained in the form of colorless prisms which melt at 13.5°C (*6*). The crystals are rhombohedral with $a = 7.30$ Å and $\alpha = 105.4$ degrees. The space group is *R*3*m* with one formula unit per cell. The structure has been determined by three-dimensional single-crystal x-ray analysis at −20°C. The water molecules form a hydrogen-bonded framework consisting of staggered columns of slightly puckered six-membered rings (Fig. 1). This arrangement is very similar to that of a single open β-hydroquinone structure (*7*) in which each benzene ring with its *para* links is replaced by a hydrogen bond. The hexamethylenetetramine molecules occupy the cavities in the framework and are surrounded by eight hexahydrate $(H_2O)_6$ rings. Each molecule, however, is hydrogen-bonded to three of these so as to hang "bat-like" to the upper wall of the cavity. The three nitrogen atoms at the top of the molecule in the figure are hydrogen-bond acceptors from the three nearest water molecules. The nitrogen at the bottom of the molecule is at distances greater than 3.6 Å from its neighboring water molecules and is not involved in hydrogen bonding.

The analogy between this structure and both the gas hydrate and hydroquinone clathrates is such that we should surely expand the concept of clathration to include this example, even though there is definite hydrogen-bonding between the host and guest species. However, this interaction is so geometrically specific to the guest species that we cannot expect to find a large isostructural series of related compounds. Rather it suggests that we may find a rational and continuous series of hydrated crystal structures, ranging from the "pure" clathrate of the gas hydrates through intermediate framework structures, such as the peralkylated ammonium salt hydrates and this structure, to those where there are hydrogen-bonded sheets, ribbons, and chains of water molecules, and finally, to those which contain isolated water molecules, as in many of the simpler hydrated salts and hydrated polar organic molecules.

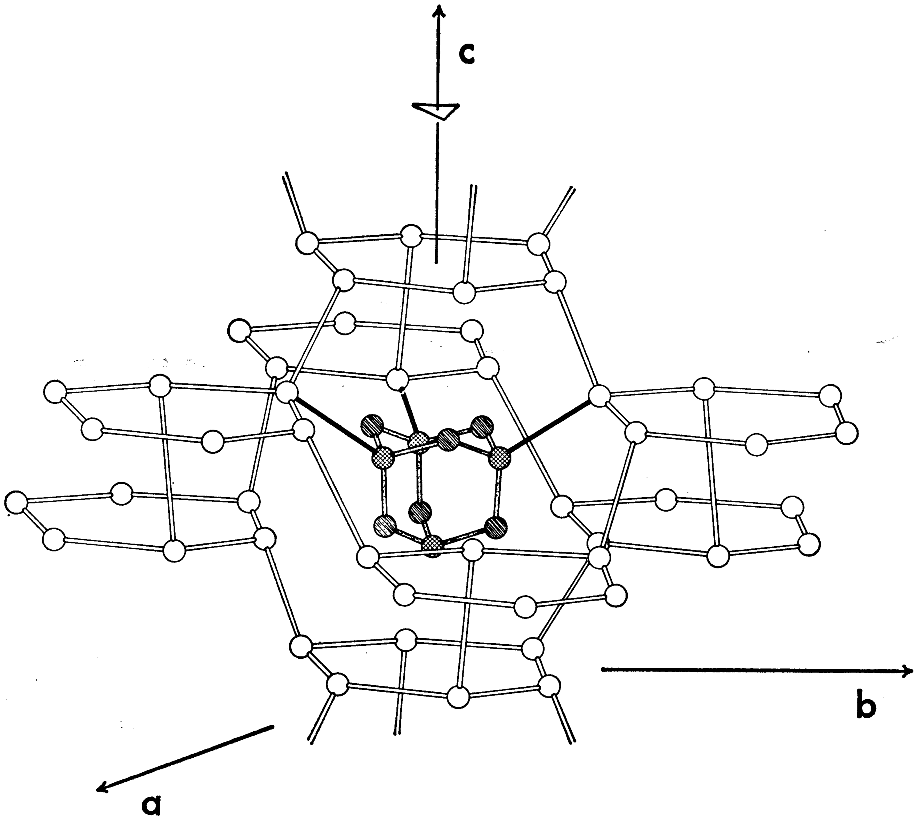

Fig. 1. Perspective diagram of the crystal structure of $(CH_2)_6N_4 \cdot 6H_2O$. The eight hexahydrate $(H_2O)_6$ rings that form the immediate surroundings of the guest molecule are shown. The oxygen, nitrogen, and carbon atoms are differentiated by shading, and the methylene hydrogens are omitted. The double and solid lines indicate O ··· H——O and N ··· H——O bonds, respectively.

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References and Notes

1. H. M. Powell, *J. Chem. Soc.* **1948**, 61 (1948).
2. L. Mandelcorn, *Chem. Rev.* **59**, 827 (1959).
3. H. M. Powell, *J. Chem. Soc.* **1950**, 298 (1950).
4. M. v. Stackelberg, *Naturwiss.* **36**, 327, 359 (1949); M. v. Stackelberg and H. R. Muller,

ibid. **38**, 456 (1951); H. R. Muller and M. v. Stackelberg, *ibid.* **39**, 20 (1952); M. v. Stackelberg and H. R. Muller, *Z. Electrochem.* **58**, 25 (1954); M. v. Stackelberg and W. Meinhold, *ibid.* **58**, 40 (1954); M. v. Stackelberg and H. Fruhbuss, *ibid.* **58**, 99 (1954); M. v. Stackelberg, *ibid.* **58**, 104 (1954); M. v. Stackelberg and W. Jahns, *ibid.* **58**, 162 (1954); M. v. Stackelberg and B. Meuthen, *ibid.* **62**, 130 (1958).

R. K. McMullan and G. A. Jeffrey, *J. Chem. Phys.* **31**, 1231 (1959); D. Feil and G. A. Jeffrey, *ibid.* **35**, 1863 (1961); M. Bonamico, G. A. Jeffrey, R. K. McMullan, *ibid.* **37**, 2219 (1962); G. A. Jeffrey and R. K. McMullan, *ibid.* **37**, 2231 (1962); R. K. McMullan, M. Bonamico, G. A. Jeffrey, *ibid.* **39**, 3295 (1963); G. Beurskens, G. A. Jeffrey, R. K. McMullan, *ibid.* **39**, 3311 (1963); P. T. Beurskens and G. A. Jeffrey, *ibid.* **40**, 2800 (1964).

6. M. Delepine, *Bull. Soc. Chim. France* **13**, 352 (1895); **17**, 110 (1897); R. Cambier and A. Brochet, *ibid.* **13**, 392 (1895).
7. D. E. Palin and H. M. Powell, *J. Chem. Soc.* **1947**, 208 (1947).
8. We thank NASA for a postdoctoral fellowship to one of us (T.C.W.M.). The work forms part of a basic research study on hydrated crystals supported by the Office of Saline Water, U.S. Department of the Interior.

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Mineralogy of Particulate Matter Suspended in Sea Water

Abstract. *X-ray diffraction analysis of the particulate matter of water samples from the Caribbean Sea, one from the surface and one from a depth of 768 meters, shows that the material has a mineral composition comparable to that found in deep-sea sediments of the area. The minerals found in the water samples include illite, the most abundant clay; kaolinite; chlorite; talc; mixed-layer clay; quartz; feldspar; and amphibole. Kaolinite and chlorite are more abundant relative to illite in the sediments than in the suspended material.*

The mineralogy of particulate matter suspended in water from the Caribbean Sea was determined for a surface sample at 12°06′N, 74°53′W (Fig. 1, location A), and for one at a depth of 768 m at 13°21′N, 64°19.5′W (Fig. 1, location B). Comparisons were made with sediment from the tops of piston cores, C 7-15 at 3515 m and C 7-7 at 3171 m, taken below the water samples. The suspended material was separated from 190 liters of sea water by means of a continuous-flow centrifuge. The weight of the analyzed sample of particulate material from 768 m was 48.9 mg (about half the total sample of suspended matter obtained). No such estimate could be obtained for the surface sample because of rust contamination from the water sampler. The mineral grains were of extremely fine size, and largely masked by organic detritus and exoskeletons. After appropriate chemical pretreatment (described below), an abundant mineral assemblage was found in the residues of both samples.

Repeated centrifuging and decanting with distilled water washed out salts and soluble organics. The carbonates were destroyed with a buffered solution of sodium acetate (*1*), the organic solids were decomposed and the manganese oxides were dissolved by hydrogen peroxide (*1*), the free iron oxides were removed by the citrate-bicarbonate-dithionite method (*1, 2*), and finally the amorphous alumina and silica were dissolved (*1, 3,*). A size separation (greater than 2 μ and less than 2 μ) was performed, and the fractions were water-sedimented onto glass slides to enhance basal lattice reflections of the layer silicates during x-ray diffraction analysis.

The weight of the mineral residue remaining after pretreatment of the suspended particulate material was on the order of a few milligrams, about 8 mg for the sample from 768 m. This material yielded diffraction spectra usable for identification purposes, but of limited value for quantitative estimates. Sometimes in x-ray diffraction analysis of the very fine layer-silicate particles, the plate-like crystals of finite thickness do not yield distinct diffraction maxima, a situation which may be thought of as extreme broadening of certain peaks. The very minute quantity of material also places limitations on the quality of the diffraction spectra.

Illite occurred in greatest abundance (probably more than 50 percent of the mineral residue) in the surface-water sample (Fig. 2, C 7-10). Second in importance was a layer-silicate mineral with peaks at 9.41 and 3.12 Å, tentatively identified as talc on the basis of comparison with x-ray powder data (*4*), with ASTM card 13-558, and with a specimen from Gouverneur, N.Y. (International Talc Co.). An uncertainty exists because pyrophyllite, the dioctahedral analogue of talc, has two strong basal spacings approximately at 9.2 and 3.04 Å (*4, 5*), also given by ASTM cards 2-0613 and 12-203. Lesser quantities of kaolinite, quartz, feldspar, amphibole, and a trace of mixed-layer clay also occurred in the surface-water sample. The occurrence of talc and amphibole in the surface-water sample and the proximity of the Magdalena River suggest a source in the metamorphic terrain of the Andes. Because of the limited quantity of material suspended in the surface-water sample, a size separation at 2 μ was not practicable.

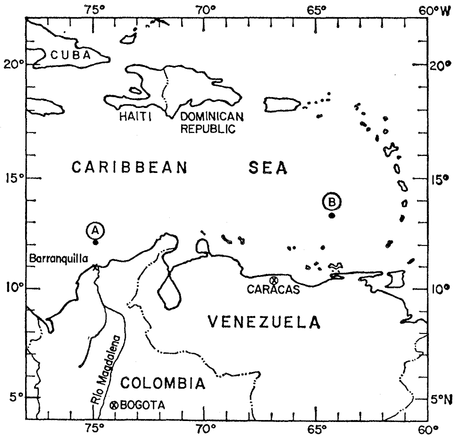

Fig. 1. Location map of samples from the Caribbean Sea for clay mineral study. Location A, 12°06′N, 74°53′W: surface-water sample C 7-10 and core C 7-15 at 3515 m. Location B, 13°21′N, 64° 19.5′W: water sample C 7-4 at 768 m and core C 7-7 at 3171 m.

Illite is also abundant in the deep-sea sediment (C 7-15) below the surface-water sample (Fig. 2), in both the greater than 2-μ and the less than 2-μ fractions. A distinct difference, however, between the mineral content of the material suspended in water and that of the bottom sediment occurs in the increase of the layer silicates with 7-Å spacings, kaolinite and chlorite. The manner in which the 7-Å peak skews to the right and the occurrence of a small peak at 7.4 Å in the greater than 2-μ fraction suggest the occurrence of another layered silicate mineral, either halloysite, known to form as a weathering product of volcanic debris on land, or a serpentine mineral, commonly found in metamorphic terrain. The lack of additional diagnostic peaks prevents a more complete identification. Talc and mixed-layer clay are present as minor constituents. Quartz, feldspar, and amphibole are plentiful, and a trace amount of gibbsite appears in both fractions.

In the water sample taken at a depth of 768 m (Fig. 3, C 7-4), illite is again the most abundant clay mineral, occurring with kaolinite, chlorite, and a minor amount of mixed-layer clay. Talc