[14] Indeed a Pc oxidized by DDQ generally shows EPR signals near $g = 2$, which is characteristic of organic radicals. See for example: P. Mu, T. Nakano, M. Handa, K. Kasuga, K. Sogabe, *Bull. Chem. Soc. Jpn*. **1991**, *64*, 3202, and references [11] and [12] therein.

[15] This property has been used, for example, to prepare stable chlorins and bacteriochlorins, see for example: A. C. Tome, P. S. S. Racerda, M. G. P. M. S. Nemes, J. A. S. Cavaleiro, *Chem. Commun.* **1997**, 1199; A. C. Tome, P. S. S. Racerda, M. G. P. M. S. Nemes, J. A. S. Cavaleiro, *Tetrahedron Lett.* **2000**, *41*, 3065.

A Dense and Efficient Clathrate Hydrate Structure with Unusual Cages**

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Clathrate hydrates, hydrogen-bonded networks of water molecules stabilized by the presence of guest molecules, are found in both natural[1] and industrial settings[2] and hence have considerable potential to affect human welfare.[3] As well, they are seen as ideal models for the hydration of hydrophobic bioorganic materials.[4] The three known hydrate structural families,[5, 6] structure (str.) I, II, and H, have the pentagonal dodecahedron (5^{12} cage) as a common feature. In fact, str. II and str. H are based on the stacking of layers of 5^{12} cages so that other polytypes are likely to exist as well.[7] Herein we report a new, highly complex hydrate structure that does not have 5^{12} polyhedra and contains two unusual cages, one of which has not been reported before. This new structure is denser than the other hydrate structures because of the low number of empty small cavities, and is likely to be a preferred structure for guests of intermediate dimensions at ambient or somewhat elevated pressures.

Dimethyl ether (DME) is one of a few guests[8, 9] that forms two distinct hydrates.[10] A phase diagram (not illustrated) shows a hydrate of composition $DME \cdot 17\,H_2O$ melting incongruently at $-20\,^{\circ}C$ (this hydrate was shown to be a str. II hydrate) and a lower hydrate of composition $DME \cdot 7\,H_2O$ melting incongruently at $-28\,^{\circ}C$. Evidence from dielectric and NMR spectroscopic measurements[11] suggested a highly anisotropic environment for the DME guest in the lower hydrate and this led to the supposition that the structure might be the same as that of the tetragonal bromine hydrate.[12] Below, we present the actual structure of the DME hydrate, which although it does have a number of cages in common with bromine hydrate, is unique and has several unusual cages.

The structure[13] of this hydrate is trigonal, space group $P321$, $a = 34.995$, $c = 12.368$ Å, and can be described as $12\,P \cdot 12\,T \cdot 24\,T' \cdot 12\,U \cdot 348\,H_2O$, where P is the $5^{12}6^3$ cage, also known from bromine hydrate, T is the well-known $5^{12}6^2$ cage from str. I hydrate, T′ is a previously unobserved cage designated as $4^15^{10}6^3$, and U is a small cage designated as $4^25^86^1$. The latter has been observed in the structure of one of the hydrates of propylamine.[5] The DME molecules reside in all three types of large cages in the structure, giving an overall composition of $DME \cdot 7.25\,H_2O$. There is no interaction between guest and host other than the van der Waals' contacts usual for the true clathrate hydrates. The T′ cage has not been recorded in either the hydrate[5] or clathrasil[14] literature, and thus this structure represents a new way[5] of filling three-dimensional space by stacking a novel combination of cages. The new hydrate falls outside the structural numbering scheme proposed by Jeffrey,[5] and we propose that the structure be known as structure T (from trigonal) hydrate.

The overall structure is shown in Figure 1, the constituent cages in Figure 2. The packing motifs resulting in the trigonal structure derive from several units with three-fold symmetry: clusters of three cages, where pairs of cages share a face so that the three have one common edge, or clusters of four where three cages are attached to a central cage by sharing a face. The guest positions in the three cages are disordered but quite well defined: a single position can be seen for each DME methyl group, whereas multiple positions are observed for the oxygen centers. As in previous work on hydrates,[15] ^2H NMR spectroscopy has shown the disorder to be dynamic. For samples corresponding to the str. II composition, the lineshape in the ^2H NMR spectrum is isotropic, as expected for DME undergoing rapid reorientation in the large pseudospherical $5^{12}6^4$ cage. Str. T shows an anisotropic lineshape

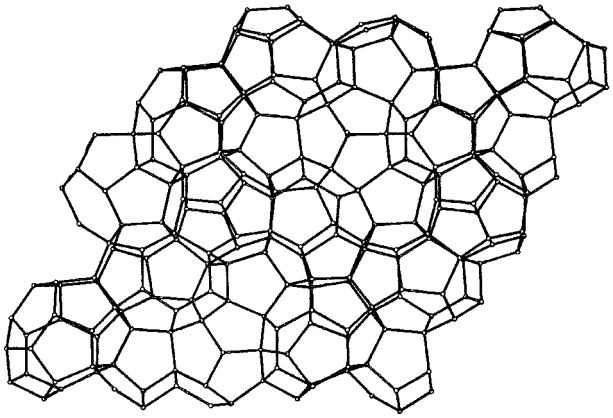

Figure 1. General view of the str. T hydrate as determined by single crystal X-ray diffraction.

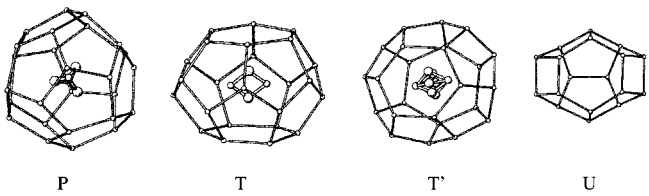

Figure 2. View of the cages in the str. T hydrate; the large cages show the location of the disordered DME guest.

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(Figure 3a) characteristic of an axially symmetric electric-field gradient at the quadrupolar nucleus, which indicates the presence of DME in nonspherical cages. The doublet splitting

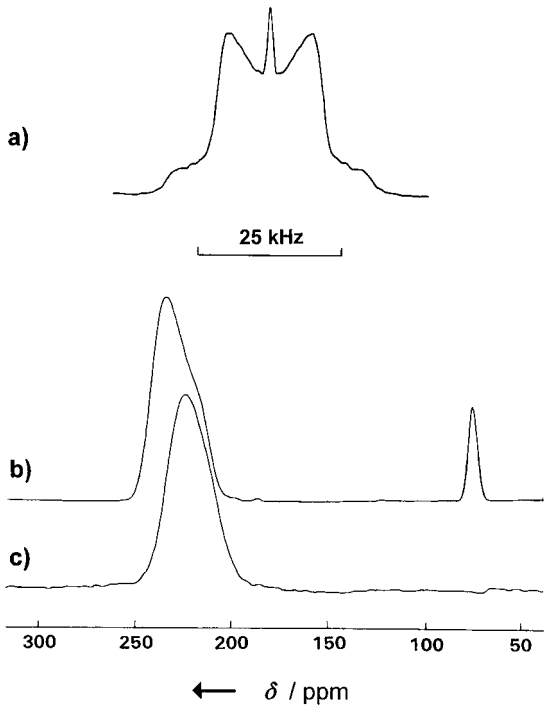

Figure 3. NMR spectra of DME hydrates: a) ^{2}H NMR spectrum at 152 K of CD_3OCH_3/H_2O, str. T; b) ^{129}Xe NMR spectrum at 77 K, DME:Xe:H_2O ratio 1:2:20, str. II; c) ^{129}Xe NMR spectrum at 77 K, DME:Xe:H_2O ratio 10:1:8.6, str. T.

of 17.5 kHz at 152 K is significantly less than the 38.5 kHz typical for a methyl group reorienting rapidly about its threefold axis. The reduction factor of 0.455 is consistent with further rapid reorientation of the whole molecule about an axis parallel to the C–C direction, as suggested by the disorder in the guest positions, with additional librational dynamics accounting for a further slight reduction.

The ^{129}Xe NMR spectra of mixed Xe/DME hydrates also provide indications of a structure different from those already known. At high water:guest ratios a spectrum (Figure 3b) is observed which is characteristic of str. II hydrates[16] with a small amount of Xe in the large cages giving the resonance at $\delta = 76$, and a strong signal at $\delta = 232$ for Xe in the small cages. When DME is in excess, however, a quite different spectrum with a signal, arising from a single small cage with a very slight asymmetry, is observed at $\delta = 222$, Figure 3c. This shift is quite different from that of Xe in small cages in other hydrate structures: it falls between the shifts for the 5^{12} cages in str. II and str. H at $\delta = 232$ and the $4^3 5^6 6^3$ cage of str. H at $\delta = 212.4$ (Xe in the 5^{12} cages of str. I and the bromine hydrate has larger shifts than str. II). Thus this new signal may be assigned to str. T.

The significance of the structure becomes apparent upon examining some of its properties. One striking feature is the relative number of small cages, the ratio of small to large cages is significantly smaller than for the other known structures. This means that if small-cage guests are absent, this structure is the most efficient in terms of minimizing vacant void space, as also reflected in the density of the hydrate structures (Table 1). The low hydrate is denser than the str. II hydrate, and also the hypothetical str. I hydrate by $\sim 2\%$, with the implication that this structure may be favored over str. I or II for guests of intermediate size at somewhat elevated pressure. It is pertinent to refer to work by Dyadin et al.[9] on the effect of pressure on the phase structure of a number of hydrates that form str. II at ambient pressure. At a few kbar pressure there is the appearance of a new phase with a hydration number of ~ 7 water molecules per guest. This was interpreted as a transition of str. II to str. I plus ice, as str. II is inherently unstable at high pressure because of the large number of empty small cages. Based on density alone, str. T should be more stable than str. I. However, there are other factors, such as hydrogen-bonded water molecules arranged in squares, that must be energetically unfavorable because of ring strain. Therefore it may be postulated that some or all of the pressure-induced transitions could involve the structure reported here.

Experimental Section

Colorless single crystals ($0.4 \times 0.4 \times 0.5$ mm) of dimethyl ether (DME) hydrate were grown in a sealed tube at $-40\,^{\circ}C$ from an aqueous solution containing excess dimethyl ether. Crystal data were collected on a Bruker SMART CCD diffractometer, (graphite monochromator) with $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å, $2\theta_{max} = < 57.5^{\circ}$, ω scan mode). The structure proved to be difficult to solve[17] as the crystal was twinned and the unit cell is large.[18]

The NMR experiments were performed as described previously.[15, 16]

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-151791. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Table 1. The distribution of large and small cages in different hydrate structures and the densities for the corresponding DME hydrates.

Hydrate	Small (S) cages[a]	Large (L) cages[a]	Ratio (S/L cages)	Density [g cm^{-3}][b]
str. H	3 (5^{12}), 2 ($4^3 5^6 6^3$)	1 ($5^{12}6^8$)	5	0.834[c]
str. II	16 (5^{12})	8 ($5^{12}6^4$)	2	0.938
str. I	2 (5^{12})	6 ($5^{12}6^2$)	0.33	1.054[c]
str. T	12 ($4^2 5^8 6^1$)	12 ($5^{12}6^3$), 12 ($5^{12}6^2$), 24 ($4^1 5^{10}6^3$)	0.25	1.074

[a] number per unit cell; [b] calculated for structure with empty small cages and large cages filled with DME; [c] hypothetical structures.

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[13] Dimethyl ether hydrate is trigonal, space group $P321$, $a = 34.995$, $c = 12.368$ Å, $\gamma = 120°$, $V = 13117.7$ Å^3, $Z = 48$, GOF on $F^2 = 0.962$. Final R indeces ($I > 2\sigma(I)$): $R_1 = 0.0538$, $wR_2 = 0.1062$ (145366 total reflections, 22397 unique).
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[18] Additional crystallographic information: Solved by direct method using the SHELXTL suite of programs.[17] TWIN matrix 010 100 00-1 was used to resolve the crystal twinning. All non-hydrogen atoms were refined anisotropically by full-matrix least squares on F^2. Hydrogen atoms in the water framework were found from the electron density map and are disordered over two positions in a hydrogen bond with a site occupancy of 0.5. Hydrogen atoms in the guest molecules were placed in calculated positions and allowed to ride on the parent atoms. All C–O and C–C bonds in guest molecules were fixed. No corrections were made for polarization or absorption.

The Oxidative Power of Protonated Hydrogen Peroxide**

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Hydrogen peroxide is an oxidant which receives much attention these days. In order to take full advantage of this environmentally friendly chemical in a large number of practical applications—for example, for bleaching in the pulp and paper industry—more effective catalysts are required.[1] Detailed mechanistic studies of simplified model systems are necessary to realize this development.

The compound H_2O_2 is unstable and decomposes into water and dioxygen (O_2) in both acidic and basic solution, as well as in the presence of transition metals.[2] Good examples of transition metal activation occur with Fenton's reagent (Fe^{2+} and H_2O_2) as well as the enzymes involved in respiration and other oxidative processes.[3–5] The fine balance between the decomposition chemistry of H_2O_2 and its action as an oxidant is quite clear, both when it is promoted by protonation or by coordination to a transition metal cation. We have recently proposed that $[HOOH]H^+$, the species most likely to be formed in acidic hydrogen peroxide solution, is a highly active oxidant in the gas phase; only 150 kJ mol^{-1} are needed to break the O–O bond.[6]

Hydrogen peroxide demonstrates extraordinary oxidative behavior in superacidic solutions: it inserts an oxygen atom into aliphatic and aromatic C–H bonds to give aldehydes/ketones or alcohols, respectively.[7–9] Theoretical calculations indicate that the reactive species is protonated hydrogen peroxide, and not free OH^+.[10] To date, no experimental evidence has been published that demonstrates the intrinsic chemical properties of $HOOH_2^+$, but it is known that this species can be formed by proton transfer in the gas phase (a rough value of 675 ± 45 kJ mol^{-1} was reported for the proton affinity (PA) of H_2O_2).[11] Herein we present the results from an experimental study of the unimolecular and bimolecular gas-phase chemistry of protonated hydrogen peroxide.

We have previously investigated the unimolecular chemistry of the isoelectronic $[H_2NNH_2]H^+$ and $[HONH_2]H^+$ systems.[12, 13] On the basis of the behavior of these ions and from a detailed quantum chemical survey of the singlet and triplet potential energy surfaces of $(H_3,O_2)^+$ we recently proposed that protonated hydrogen peroxide in its singlet ground state will preferably lose an oxygen atom according to the spin change mechanism [Eq. (1)].[6]

$$\begin{aligned} {}^1HOOH_2^+ &\rightarrow {}^1HO\cdots OH_2^+ \rightarrow {}^3HO\cdots OH_2^+ \\ &\rightarrow {}^3O\cdots H_3O^+ \rightarrow {}^3O + H_3O^+ \end{aligned} \quad (1)$$

We have now conducted experiments on a grand-scale magnetic sector tandem mass spectrometer to verify this prediction. A pure beam of $[HOOH]H^+$ ions (m/z 35.01) was selected using the first mass spectrometer of the tandem combination. A small fraction of these ions, with energies close to the threshold value for reaction (the so-called metastable ions), decompose spontaneously during passage through the field-free region preceding the second mass spectrometer, and the fragment ions were registered by scanning the second electric sector. The spectrum obtained is shown in Figure 1. the spectrum contains only one significant peak, namely for H_3O^+, which corresponds to the loss of one oxygen atom, and is in complete agreement with the theoretical predictions. The maximum amount of energy available to the $HOOH_2^+$ ions produced in the ion source

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