

Structure, Stoichiometry, and Morphology of Bromine Hydrate<sup>†</sup>Konstantin A. Udachin,<sup>‡</sup> Gary D. Enright, Christopher I. Ratcliffe, and John A. Ripmeester\*

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**Abstract:** The hydrate of bromine was one of the first clathrate hydrates discovered. It has played a significant role in the development of the solid solution theory of clathrate hydrates, yet its detailed structure remains unknown. This hydrate again has become a test case for two different views of clathrates: the solid solution model, after van der Waals and Platteuw, that sees clathrates as unstable lattices which derive stability from a minimum degree of cage filling and thus are nonstoichiometric, and a view promoted by Dyadin and Aladko that all large cages in a hydrate structure need to be filled. In light of the latter view, existing data obtained over the last ~160-year period on the composition and morphology of bromine hydrate would require the existence of four different hydrate structures. Our single crystal diffraction study of 16 different crystals of distinct compositions ( $\text{Br}_2 \cdot 8.62\text{H}_2\text{O}$  to  $\text{Br}_2 \cdot 10.68\text{H}_2\text{O}$ ) and morphologies showed that there is just a single structure (tetragonal,  $P4_2/mnm$ ,  $a = 23.04 \text{ \AA}$ ,  $c = 12.07 \text{ \AA}$ , the structure originally proposed by Allen and Jeffrey) with considerable variation in the degree of occupancy of the large cages. The results favor the solid solution model for clathrates, and settle the question of long standing regarding the structure(s) of bromine hydrate. The bromine atoms occupy the large 14- and 15-hedral cages with up to 15 different crystallographically independent sites per cage and fractional occupancies from 0.19 to  $< \sim 0.01$ . The bromine hydrate structure is unique, so far.  $^{129}\text{Xe}$  NMR results suggest that when attempts were made to produce a double hydrate of bromine and xenon, a transient cubic structure II hydrate resulted, which slowly converted to the tetragonal form.

## Introduction

In recent years the existence of large deposits of natural gas hydrates has again brought to the fore the need to develop accurate models to predict the stability limits of the deposits, the gas content of such deposits, and the potential impact on the global environment.<sup>1</sup> Fundamental to the development of good prediction models is the need for good structural data and some certainty that the clathrate hydrate concepts developed some time ago still are the most suitable.

Bromine hydrate (1) was one of the first clathrate hydrates discovered, and it has played a significant role in the development of models for all clathrate hydrates. It is remarkable that its detailed structure remains unknown, and that today again bromine hydrate is at the heart of a challenge to the commonly accepted model for clathrate hydrates.

A solid of composition  $\text{Br}_2 \cdot 10\text{H}_2\text{O}$  was first recognized as a distinct phase by Lowig<sup>2</sup> and reported in 1828. Since then, a significant number of scientists have studied compositions in this system with a considerable variability in results<sup>2–14</sup> (see

Table 1. Summary of Bromine Hydrate Composition Data

author	year	hydration no.	method	ref
Lowig	1829	10	Ch	2
Alekseev	1876	10	Ch	3
	1879	10	Ch	4
Roozeboom	1884	10	Ch	5
Giran	1914	8	Ch, Th	6
Bouzat	1923	6	F	7
Harris	1932	10	Sc	8
D'Ans and Hofer	1934	8	Cm	9
Mulders	1937	8.47	F	10
		8.36		
Zernike	1947	7	Sc	11
Allen and Jeffrey	1963	8.6	X-ray	12
Dyadin and Aladko	1977	12	Sc	13
		10		
		8.3		
		7		
Cady	1986	7.9		14

<sup>a</sup> Source: Dyadin and Aladko.<sup>13</sup> Ch, chemical; Th, Thermal; F, Forcrand; Cm, Cameron; Sc, Schreinemakers.

Table 1). As noted above, bromine hydrate has played a significant but somewhat misleading role in the development of a thermodynamic model for clathrate hydrates. The first attempt to study the hydrate by X-ray powder diffraction by von Stackelberg and Muller gave results that were interpreted in terms of the cubic structure I hydrate (Str.I).<sup>15</sup> This information together with hydration numbers determined by

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Mulders<sup>10</sup> were used by van der Waals and Platteeuw in their "solid solution" model for clathrate hydrates<sup>16</sup> to derive a value of the free energy difference ( $\Delta\mu$ ) between the hypothetical empty Str.I hydrate lattice and normal ice. Although, in light of more recent information, including the work reported here, the bromine hydrate structure is known not to be Str.I, and therefore the value found for  $\Delta\mu$  erroneous, the solid solution model has withstood the test of time with few real challenges to its validity. Again, the current challenges involve bromine hydrate.

Briefly stated, the solid solution model assumes that the empty hydrate lattice is unstable with respect to that of ice, and that stability is imparted to the lattice by a minimum degree of cage filling. The model predicts, in general, that hydrates are nonstoichiometric, and that there is a direct relationship between  $\Delta\mu$  and the occupancy numbers of the different cages in the hydrate structure. Although generally confirmed, this has been difficult to test experimentally, as the  $\Delta\mu$  values found predict that the large cages in both Str.I and Str.II hydrates should be nearly completely filled, and the accuracy of experimental cage occupancy determinations has not been sufficient to distinguish full from nearly full cages (e.g. occupancy fractions of  $\sim 0.95$  vs 1.0).<sup>17,18</sup>

Allen and Jeffrey<sup>12</sup> first showed that there is at least one bromine hydrate structure,  $\text{Br}_2 \cdot 8.6\text{H}_2\text{O}$ , that does not have the cubic Str.I hydrate lattice. Although the lattice symmetry and unit cell parameters for this tetragonal structure were given, atomic coordinates were not reported.<sup>12</sup> However, the water framework was surmised to be closely related to that of the tetragonal hydrate of tetra-*n*-butylammonium fluoride,  $5(n\text{-C}_4\text{H}_7)_4\text{N}^+\text{F}^- \cdot 164\text{H}_2\text{O}$ , where some of the usual clathrate hydrate cages are fused to form the larger spaces in which the cations are located.<sup>20</sup> If we consider the hydration numbers reported over the years for the bromine-water system, it is easy to come to the conclusion that perhaps several bromine clathrate hydrate exist. This is central to the view of Dyadin and Aladko,<sup>13,19</sup> who have promoted a concept of clathrates that requires complete filling of the large cavities in all clathrate hydrate structures. In this situation several different hydrates varying in structure and composition must exist.<sup>13,19</sup> The authors have analyzed the available literature data and carried out their own study on hydration numbers. A statistical treatment of all data resulted in the following hydrate compositions:  $\text{Br}_2 \cdot 6.98\text{H}_2\text{O}$ ,  $\text{Br}_2 \cdot 8.32\text{H}_2\text{O}$ ,  $\text{Br}_2 \cdot 10\text{H}_2\text{O}$ , and  $\text{Br}_2 \cdot 12\text{H}_2\text{O}$ . On the basis of these stoichiometries, Dyadin and Aladko have suggested a number of possible bromine hydrate structures: a hexagonal structure with the parameters  $a = 12.4 \text{ \AA}$  and  $c = 12.5 \text{ \AA}$ , an orthorhombic structure with the parameters  $a = 23.5 \text{ \AA}$ ,  $b = 19.9 \text{ \AA}$ ,  $c = 12.1 \text{ \AA}$ , a cubic (str.I hydrate) structure with  $a = 12 \text{ \AA}$ , and a hydrate of an unknown structure with composition  $\text{Br}_2 \cdot 12\text{H}_2\text{O}$ . This conjecture is reasonable in light of the observation that crystals of different hydration numbers had remarkably different morphologies, and in some cases, different colors. On the other hand, the "solid solution" model would allow for varying degrees of occupancy of the large cavities in the structure of a single hydrate. Therefore, the existence of a single versus multiple structures has a number of important

**Table 2.** Crystal and Structure Refinement Data

compd	<b>1</b>
formula	$\text{Br}_{1.89} \cdot 8.6\text{H}_2\text{O}$
fw	306.13
temp, K	173
cryst size, mm	$0.3 \times 0.3 \times 0.4$
cryst system	tetragonal
space group	$P4_2/mnm$
$a$ , $\text{\AA}$	23.0436(9)
$c$ , $\text{\AA}$	12.0745(7)
$V$ , $\text{\AA}^3$	6411.7(5)
$Z$	20
$\rho_{\text{calc}}$ , $\text{g cm}^{-3}$	1.586
diffractometer	Siemens SMART CCD
radiation	Mo K $\alpha$
total no. of rflns	24788 ( $R_{\text{int}} = 0.053$ )
no. of unique rflns	2549
no. rflns $I > 2\sigma(I)$	2494
no. parameters	453
$R$	0.047
$R_w$	0.0707
GOF	1.018
resid density, $\text{e \AA}^{-3}$	0.651 and $-0.225$

**Table 3.** The Large Cage Occupancy and Structure Refinement Data for Various Crystals Studied

initial composition of soln	large cage occupancy	hydrate stoichiometry	no. of unique reflcns	$R$ for refl $> 4\sigma$
$\text{Br}_2 \cdot 20\text{H}_2\text{O}$	0.805	$\text{Br}_2 \cdot 10.68\text{H}_2\text{O}$	2512	0.090
$\text{Br}_2 \cdot 14\text{H}_2\text{O}$	0.914	$\text{Br}_2 \cdot 9.41\text{H}_2\text{O}$	4482	0.076
$\text{Br}_2 \cdot 10\text{H}_2\text{O}$	0.946	$\text{Br}_2 \cdot 9.09\text{H}_2\text{O}$	2549	0.047
$\text{Br}_2 \cdot 7\text{H}_2\text{O}$	0.962	$\text{Br}_2 \cdot 8.94\text{H}_2\text{O}$	2551	0.072
$\text{Br}_2 \cdot 5\text{H}_2\text{O}$	0.998	$\text{Br}_2 \cdot 8.62\text{H}_2\text{O}$	2504	0.091

implications central to the fundamental understanding of clathrate hydrates and the validity of the solid solution model.

Another point that should be made is that for just about all known guests which form simple hydrates (about 140) there is a reasonably straightforward relationship between guest size and hydrate structure.<sup>21</sup> On the basis of this criterion, bromine should form a structure II hydrate.

We have studied the system  $\text{Br}_2\text{-H}_2\text{O}$  by X-ray single crystal diffraction, expecting to find bromine hydrates of unknown structure. We also have used  $^{129}\text{Xe}$  NMR to explore the possibility of producing other hydrate structures by including xenon in a double hydrate structure<sup>21</sup> along with bromine.

## Experimental Section

Single crystals of bromine hydrate were grown from distilled water and bromine ("Baker analyzed" grade of purity 99.5%) at temperatures from  $-5$  to  $+5$  °C. The hydrate single crystals were removed from solution at 0 °C, placed into thin-walled glass capillaries at  $-20$  °C, and analyzed by the X-ray technique. The experiments were carried out on a Siemens SMART CCD diffractometer with use of Mo K $\alpha$  radiation and a graphite monochromator. All experimental data for one single crystal are given in Table 2. Some experimental data for other crystals studied are given in Table 3. The structure was solved and refined with the program SHELXTL.<sup>22,23</sup> All oxygen atoms were refined with anisotropic thermal parameters. The hydrogen atoms of the water molecules were located on a Fourier difference map.

Samples of double hydrates of Xe and  $\text{Br}_2$  for  $^{129}\text{Xe}$  NMR experiments were prepared at several ratios:  $0.1\text{Xe}:0.9\text{Br}_2:8.4\text{H}_2\text{O}$ ,  $0.4\text{Xe}:0.6\text{Br}_2:8.4\text{H}_2\text{O}$ , and  $0.6\text{Xe}:0.8\text{Br}_2:8.4\text{H}_2\text{O}$ . Xe gas was condensed onto crushed ice and bromine in 10 mm o.d. Pyrex tubes on a vacuum line at 77 K. The tubes were sealed and the samples conditioned in dry ice and then ice baths. The sealed tubes were used directly in the

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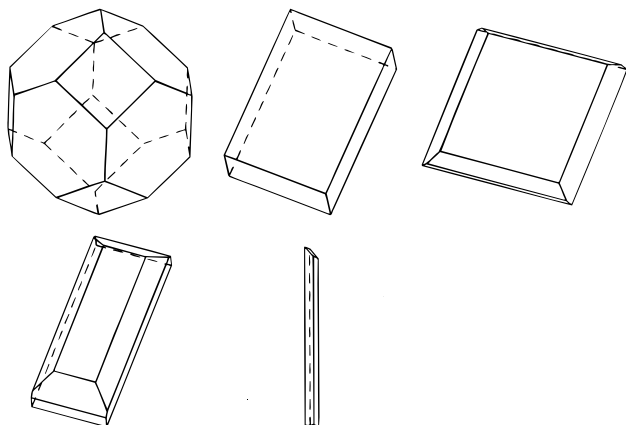
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**Figure 1.** Single crystals of different morphology found for the  $\text{Br}_2\text{-H}_2\text{O}$  system.

static-sample NMR experiments. Samples for magic angle spinning (MAS) had to be extracted from the tubes after conditioning and transferred to spinners at low temperature.  $^{129}\text{Xe}$  NMR spectra were obtained at 49.79 MHz on a Bruker CXP-180 spectrometer. Static-sample spectra at 77 K were obtained by using a cross-polarization sequence in a probe where the horizontal coil and sample were immersed in liquid nitrogen. Static-sample spectra at higher temperatures were obtained by using a Bruker variable-temperature probe with a flow of cold nitrogen gas and a B-VT 1000 temperature controller. Magic angle spinning (MAS) spectra at several temperatures above 200 K were obtained by using a Doty Scientific variable-temperature CP/MAS probe (7 mm sapphire rotors, spinning rates about 2.5 kHz). All samples were cold-loaded into the probes.

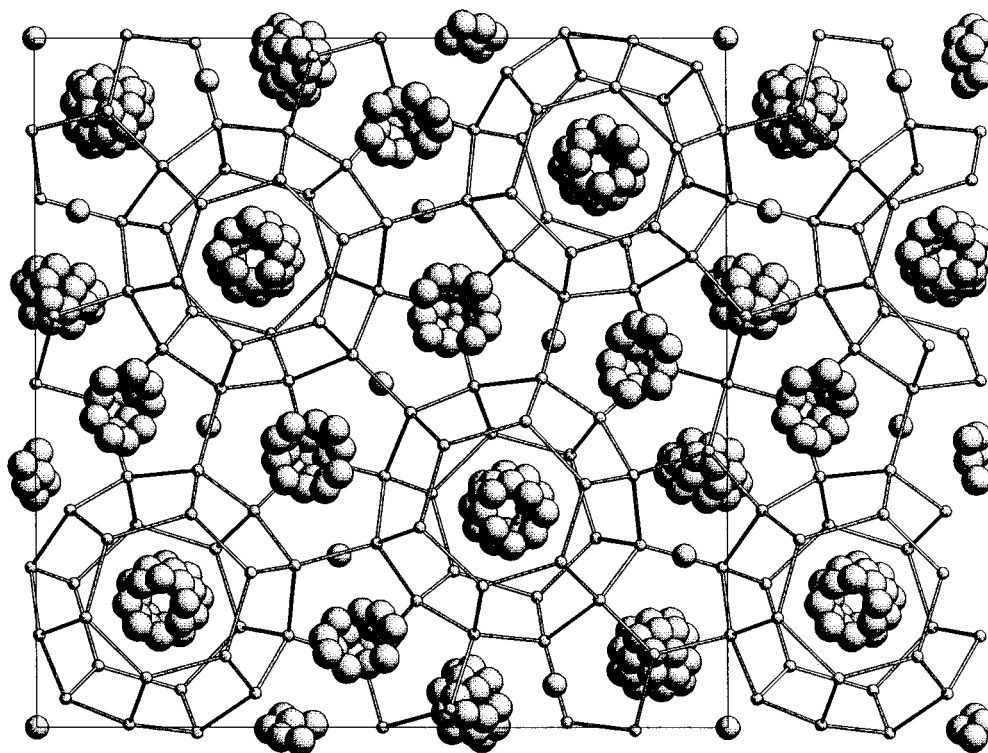
## Results and Discussion

**(a) The Crystal Structure.** Sixteen single crystals of bromine hydrate, grown from reaction mixtures with different  $\text{Br}_2\text{:H}_2\text{O}$  ratios from 1:5 to 1:20 (there are two liquid phases since bromine has limited solubility in water), were studied. The crystals were grown at different rates: fast (over several hours) or slow (over 4 months). The crystals were grown both

from solution and via vapor diffusion, the latter in the cases with bromine in excess of  $\text{Br}_2\cdot 8.6\text{H}_2\text{O}$ . The unit cell parameters of all 16 crystals were measured and complete X-ray structural analyses of six of these were carried out. The crystals had a variety of shapes that depended on the growing conditions. Figure 1 shows the most typical crystal morphologies. Crystals obtained from dilute solution usually were octahedral; crystals grown from solutions of composition close to  $\text{Br}_2\cdot 9\text{H}_2\text{O}$  had slab-like shapes typical of tetragonal hydrates; crystals grown from solutions with excess bromine (via the vapor phase) acquired the shape of needles with a square cross section. In solution the crystals were light brown, whereas the needlelike crystals were dark brown.

Despite having different morphologies all of the crystals studied proved to be hydrates of the tetragonal structure with the space group  $P4_2/mnm$ . Figure 2 presents a general view of the structure. The cell has 172 water molecules that are hydrogen bonded to form the clathrate framework. The  $\text{O}\cdots\text{O}$  distances vary from 2.69 to 2.90 Å, and the  $\text{O}\cdots\text{O}\cdots\text{O}$  angles between the hydrogen bonds vary from 100.6 to 122.3°. Fractional atomic coordinates of the water molecules are given in Table 4. The water framework contains sixteen 14-hedral cavities  $5^{12}6^2(\text{T})$ , four 15-hedral cavities  $5^{12}6^3(\text{P})$ , and ten dodecahedral cavities  $5^{12}(\text{D})$  in the unit cell. There are two distinct types of D cavities,  $2\text{D}_\text{A}$  and  $8\text{D}_\text{B}$ , which make up two five-D-cavity fragments typical of this structure (Figure 3). There are also two distinct types of T cavities per cell: 8 cavities designated as  $\text{T}_\text{A}$  that are connected with each other by hexagons and form columns along the  $c$  axis, and 8 designated as  $\text{T}_\text{B}$  which are paired along the  $4_2$  axis (Figure 4). The overall formula in terms of cages per unit cell is then  $2\text{D}_\text{A}8\text{D}_\text{B}8\text{T}_\text{A}8\text{T}_\text{B}4\text{P}\cdot 172\text{H}_2\text{O}$ . This is consistent with Allen and Jeffrey's surmised structure.<sup>12</sup>

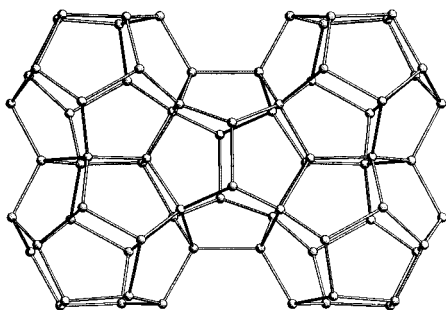
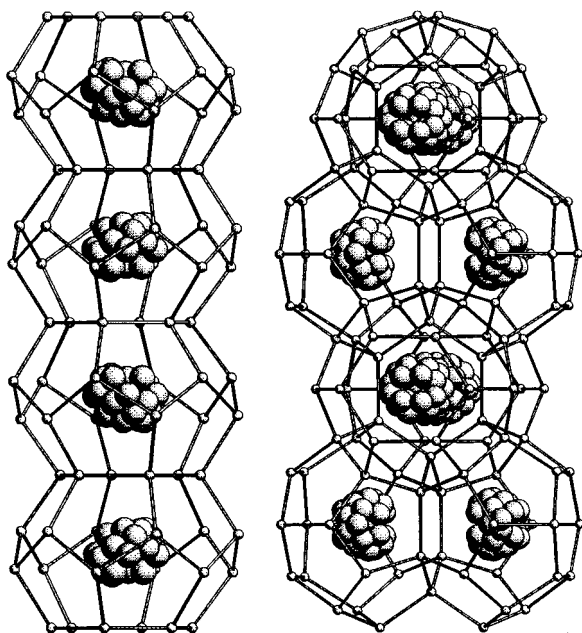
The bromine molecules are located in the large T and P cavities while the small dodecahedral cavities are vacant or partially occupied by  $\text{O}_2$  or  $\text{N}_2$  molecules that are incorporated during crystallization in air. The bromine molecules are disordered in such a way that it is possible to determine 14



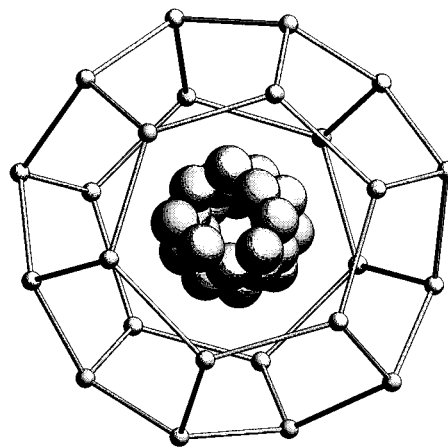
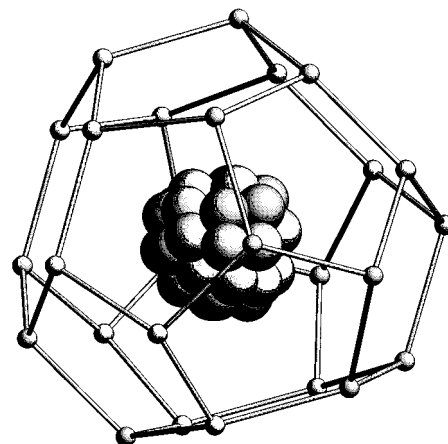
**Figure 2.** General view of the bromine hydrate structure. View approximately along the  $z$  axis (hydrogen atoms are omitted).

**Table 4.** Fractional Atomic Coordinates of Water Oxygens ( $\times 10^4$ ) and Equivalent Isotropic Displacement Parameters

atom	x	y	z	$U(\text{eq})$
O1	1036(4)	2750(5)	0	36(2)
O2	494(3)	3166(2)	-1842(4)	33(1)
O3	1322(3)	3642(3)	-3196(5)	37(2)
O4	5556(5)	2915(4)	0	34(2)
O5	6456(5)	2066(7)	0	36(2)
O6	56(3)	1343(3)	1829(6)	39(2)
O7	898(3)	898(3)	5000	34(2)
O8	425(2)	425(2)	3070(9)	30(2)
O9	-1066(3)	1066(3)	1108(7)	33(2)
O10	1589(5)	722(4)	0	35(2)
O11	2680(3)	4923(3)	1928(5)	31(1)
O12	2245(4)	3107(3)	0	35(2)
O13	3743(2)	2350(2)	1943(3)	29(1)
O14	5978(2)	269(2)	1176(4)	33(1)
O15	7595(6)	2405(6)	0	38(4)
O16	8150(3)	1850(3)	1808(8)	34(2)
O17	0	5000	2500	33(2)

**Figure 3.** Five-D-cavity fragment in the hydrate framework. View approximately along the  $z$  axis (hydrogen atoms are omitted).**Figure 4.** The 14-hedral cavities (left)  $T_A$  and (right)  $T_B$ .

crystallographically independent sites for the bromine atoms in the  $T_A$  cavity, 15 sites in the  $T_B$  cavity, and 12 sites in the P cavity. The distance between the bromine atom positions ranges from 2.25 to 2.38 Å and was obtained under the requirement that each bromine atom must be connected to another bromine atom. The likely locations of the molecule in the  $T_A$  cavity are shown in Figure 5. It should be noted that there are no bromine sites along the axis going through the centers of the hexagonal sides of the cage. This might be due to the fact that the  $T_A$  cavity is slightly compressed along this axis, which makes it

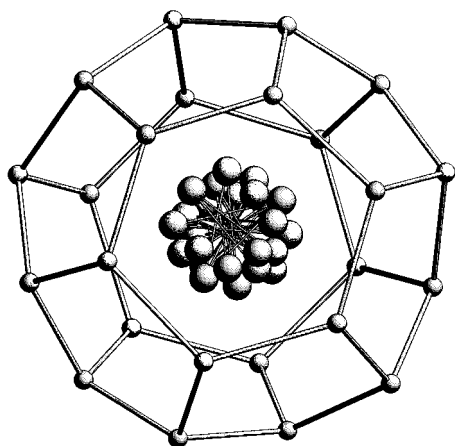
**Figure 5.** Disordering of the  $\text{Br}_2$  molecule in the  $T_A$  cavity.**Figure 6.** Disordering of the  $\text{Br}_2$  molecule in the P cavity.

impossible for the bromine molecule to be located there. Bromine molecules are arranged in a somewhat different way in the  $T_A$  and  $T_B$  cages although they have the same symmetry  $m$ . This means that the bromine atoms have a different number of positions and a different distribution over these positions. So, two 14-hedral cavities, which have the same symmetry are crystallographically distinct and have different types of disorder for the encaged bromine molecules. Disordering of the bromine molecule in the P-cavity is illustrated in Figure 6.

The minimum intermolecular Br—O distance is 3.1 Å, and the intermolecular distance between two bromine molecules in different cavities is 4.2 Å. The bromine molecule occupies several crystallographically independent sites in each of the T and P cavities and the degree of occupancy of these sites is between 0.01 and 0.19. The locations of the bromine atoms are the same for the crystals grown under different conditions. However, the site occupancies differ, resulting in different degrees of cavity filling and, therefore, different hydration numbers for the crystals. Table 5 presents the coordinates of the bromine atoms and their site occupancies. The site occupancy data were used to calculate the cage occupancy (Table 5). The large cage occupancies vary from 0.80 for crystals grown from solutions of composition  $\text{Br}_2:20\text{H}_2\text{O}$  to 1.0 for crystals grown with excess bromine via the vapor phase. The data obtained can explain all of the experimental composition data that have been obtained over the last ~160 years. Hydration numbers greater than 8.6 can be attributed to hydrates in which the large cavities are not completely occupied. Hydration numbers smaller than 8.6 may be explained by the absorption of excess molecular bromine on the surface of the crystal. We have already mentioned that the needle-like crystals

**Table 5.** Fractional Coordinates of Bromine Atoms, Site Occupancies, and Degree of Filling of the Large Cavities

atom	X	Y	Z	site occupancy	thermal parameters	multiplicity	deg of cavity filling
BR1A	0.69662	0.27596	0.29874	0.19865	0.028	16	T <sub>A</sub> 0.926
BR2A	0.66098	0.35396	0.19780	0.16064	0.029	16	
BR3A	0.64581	0.31365	0.18535	0.14307	0.029	16	
BR4A	0.70726	0.29274	0.31785	0.12156	0.028	8	
BR5A	0.65990	0.34010	0.17429	0.11129	0.027	8	
BR6A	0.71493	0.32202	0.32071	0.09152	0.029	16	
BR7A	0.63282	0.32219	0.23961	0.04783	0.034	16	
BR8A	0.71829	0.28171	0.26694	0.04414	0.029	8	
BR9A	0.70809	0.34875	0.29996	0.02853	0.033	16	
BR0A	0.70655	0.36203	0.22363	0.03084	0.033	16	
BR1K	0.66327	0.27177	0.26334	0.03183	0.033	16	
BR2K	0.64724	0.35276	0.24607	0.02349	0.035	8	
BR3K	0.73439	0.30955	0.24176	0.02270	0.036	16	
BR4K	0.71133	0.33903	0.18206	0.02023	0.034	16	
BR1B	0.91199	0.55226	-0.04959	0.09911	0.031	16	
BR2B	0.88471	0.57096	0.06118	0.09545	0.031	16	
BR3B	0.83301	0.52923	-0.04995	0.08428	0.030	16	
BR4B	0.86724	0.49307	-0.05263	0.08360	0.034	16	
BR5B	0.88976	0.54418	0.09456	0.08230	0.031	16	
BR6B	0.88111	0.51732	-0.09309	0.07745	0.034	16	
BR7B	-0.01397	0.35355	0.57657	0.07618	0.031	16	
BR8B	0.83627	0.50314	-0.03015	0.07041	0.033	16	
BR9B	0.84634	0.56761	0.04329	0.06653	0.034	16	
BR0B	0.86185	0.55368	-0.07982	0.06369	0.035	16	
BR1L	0.89986	0.49659	0.03916	0.05855	0.034	16	
BR2L	0.90786	0.52275	0.07312	0.07087	0.032	16	
BR3L	0.85535	0.48519	0.00000	0.05974	0.036	8	
BR4L	0.87245	0.58460	0.01638	0.05624	0.032	16	
BR5L	2.10529	-2.57741	0.00000	0.03385	0.032	8	
BR1C	-0.36011	-0.42299	0.95057	0.08840	0.034	16	
BR2C	-0.39107	-0.42040	0.91803	0.07463	0.037	16	
BR3C	-0.39964	-0.36071	0.92851	0.07445	0.036	16	
BR4C	-0.38774	-0.34827	0.96153	0.07103	0.034	16	
BR5C	-0.44060	-0.40431	0.96160	0.06798	0.035	16	
BR6C	-0.42401	-0.42401	0.94125	0.04836	0.036	8	
BR7C	-0.39054	-0.39054	0.89802	0.03792	0.038	8	
BR8C	-0.37075	-0.37075	0.92810	0.03044	0.035	8	
BR9C	-0.43745	-0.36939	0.00000	0.02529	0.033	8	
BR0C	-0.65297	0.41758	0.00000	0.01440	0.029	8	
BR1M	-0.35978	-0.35978	0.00000	0.01053	0.033	4	
BR2M	-0.43242	-0.43242	0.00000	0.00839	0.036	4	

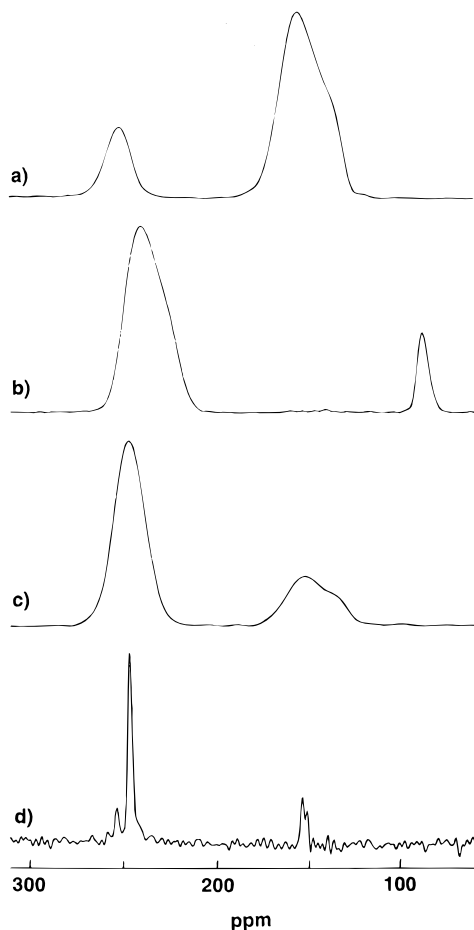
**Figure 7.** Possible connections between bromine atoms in the T<sub>A</sub> cavity.

grown in the presence of excess bromine are of a more intense color. Surface adsorption perhaps also can explain the formation of needlelike crystals, as it is likely that the preferential sorption of bromine on some of the crystal faces inhibits growth in those directions.

**(b) NMR Results.** Prior to the single crystal X-ray work we studied several mixed Br<sub>2</sub>/Xe hydrate samples using <sup>129</sup>Xe NMR. Taken on their own these results offered clues that the proposed tetragonal structure of Jeffrey was likely correct, but

they did not provide conclusive evidence. Now, in light of the new single crystal X-ray data, it is pleasing to find that the <sup>129</sup>Xe results are quite consistent with the tetragonal structure.

Figure 8 shows a comparison of the 77 K <sup>129</sup>Xe NMR CP spectra for Str.I Xe hydrate, a Str.II Xe/benzene mixed hydrate, and a mixed Br<sub>2</sub>/Xe hydrate. At 77 K (Figure 8c) we observe two broad resonances from Xe, one at 244 ppm which can be assigned to Xe in the small 12-hedral cage, which is significantly stronger than the second, at 147 ppm (isotropic shift), corresponding to Xe in the large 14-hedral cage. This arrangement of intensity is opposite to that found for pure Xe hydrate (where the intensities are about 1:4 S:L, since the small cages are not fully occupied in the equilibrated structure), clearly showing that this material is different from Xe Str.I hydrate. The line due to Xe in the small cages has a shift between those for Str.I (250 ppm) and Str.II (235 ppm), furthermore the MAS spectrum at 245 K (Figure 8d) reveals that there are in fact two resonances, at 253 and 256 ppm, in the small cage region with a roughly 1:4 intensity ratio, as would be expected for the 2D<sub>A</sub>:8D<sub>B</sub> small cages of the tetragonal structure. The anisotropic line in the 147-ppm region (at 77 K) is very similar in shape to that of the 14-hedral cage of Str.I (isotropic shift 148 ppm at 77 K). Also, the breadth of the line at 153 ppm (at 245 K) in the MAS spectrum hints at a slight difference in isotropic shift for Xe in the T<sub>A</sub> and T<sub>B</sub> cages. We would have expected Xe in the 15-hedra to have a shift between that of the 14-hedron



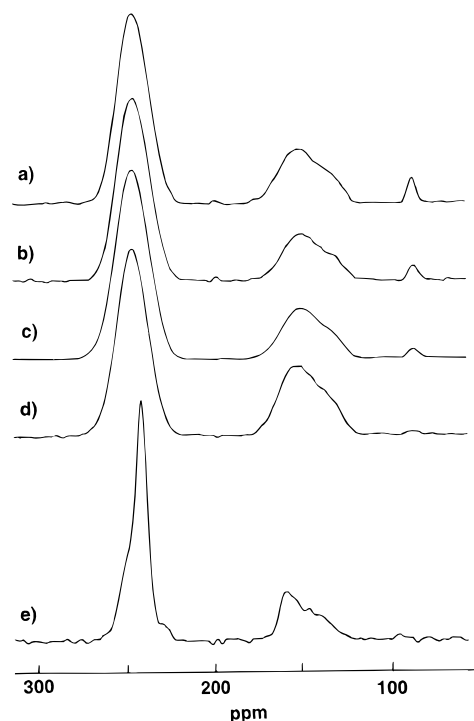
**Figure 8.**  $^{129}\text{Xe}$  NMR spectra: (a) Xe Str.I hydrate at 77 K, static,  $t_{\text{CP}} = 20$  ms; (b) Xe/benzene Str.II hydrate at 77 K, static,  $t_{\text{CP}} = 20$  ms; (c) Xe/ $\text{Br}_2$  hydrate (0.4:0.6:8.4 $\text{H}_2\text{O}$ ) at 77 K, static,  $t_{\text{CP}} = 20$  ms; and (d) Xe/ $\text{Br}_2$  hydrate (0.4:0.6:8.4 $\text{H}_2\text{O}$ ) at 245 K, magic angle spinning, no CP,  $^1\text{H}$  decoupled.

(147 ppm at 77 K) and the 16-hedron of Str.II (86 ppm at 77 K for the benzene/Xe Str.II shown) and it ought to show a chemical shift anisotropy; no such signals are apparent. (Possible reasons include the following: a preferred  $\text{Br}_2$  occupancy of the relatively few cages of this type; a large anisotropy of the chemical shift; and an accidental coincidence of the shift and anisotropy with that of xenon in the 14-hedron.)

One surprising observation from the  $^{129}\text{Xe}$  NMR studies is that the samples shortly after preparation usually showed a weak isotropic line at 86.5 ppm (at 77 K) characteristic of Xe in the large cage of Str.II hydrates. However, in all cases this line gradually disappeared with further conditioning over an extended period of time, Figure 9. It thus appears that the Xe/ $\text{Br}_2$  combination can support a hydrate of Str.II but that this is metastable with respect to the tetragonal structure. Since there is no evidence from the crystallography for a Str.II hydrate with  $\text{Br}_2$  alone, we suggest that the ability of Xe to occupy small hydrate cages permits the transient formation of Str.II with  $\text{Br}_2$  occupying a large fraction of the large cages.

## Conclusions

Instead of forming a number of different hydrate structures as suggested recently, bromine hydrate,  $\text{Br}_2 \cdot n\text{H}_2\text{O}$  is shown to



**Figure 9.** (a–d)  $^{129}\text{Xe}$  NMR static CP spectra ( $t_{\text{CP}} = 20$  ms) at 77 K of the 0.6Xe:0.8 $\text{Br}_2$ :8.4 $\text{H}_2\text{O}$  sample at different times after preparation: (a) 6 h; (b) 23 h; (c) 41 h; (d) 64 h. The sample was annealed in an ice bath for the first 23 h and thereafter in dry ice. (e) Static CP spectrum ( $t_{\text{CP}} = 0.7$  ms) at 200 K obtained at 43 h.

form only a tetragonal hydrate, space group  $P4_2/mnm$ ,  $a = 23.04$  Å,  $c = 12.07$  Å. Hydration numbers  $n$  reported in the literature range from 6 to 12. For the crystals studied here  $n$  ranges from 8.62 to 10.68 (as determined from the structural data), and this is shown to be due to variable occupancy of the large cages in the structure. The results obtained finally define the details of the hydrate lattice and explain data collected over the last ~160 years. The variable occupancy of the large cages is in general agreement with van der Waals and Platteeuw's "solid solution" model for clathrates. There still are challenges in understanding why only the bromine guest gives a tetragonal structure, as just about all other simple guests promote either structure I or II hydrate (*tert*-butylamine is an exception, and indications are that the lower hydrate of dimethyl ether also has a unique structure). The crystal morphologies and hydration numbers are shown to be linked, the common cause likely being the different concentrations of the starting solutions.

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**Supporting Information Available:** Tables of crystal data and structure refinement, atomic and hydrogen coordinates and equivalent isotropic displacement parameters, anisotropic displacement parameters, and bond distances and angles for **1** (10 pages). See any current masthead for ordering and Internet access instructions.

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