Supplementary Information for:

Anisotropy of Dodecahedral Water Cages for Guest Gas Occupancy in Semiclathrate Hydrates

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1. Experimental details

The materials used in this study were TBAB (Sigma-Aldrich, 99 in mole fraction), Xe gas (Tokyo Rare Gases, >0.99999 in mole fraction), Kr gas (Tokyo Rare Gases, >0.99999 in mole fraction) and Ar gas (Taiyo Nippon Sanso, >0.99999 in mole fraction). Water was sterilized by ultraviolet ramp and filtrated by activated carbon.

The single crystals were formed in a high pressure cell equipped with glass windows. The formation conditions of the single crystals are summarized in Table S1. An aqueous solution of TBAB was gravimetrically prepared with the aid of electronic balance (A&D, GX-6100). The aqueous solution was injected into the high pressure cell. The cell was immersed in a bath filled with a propylene glycol aqueous solution. The bath temperature was controlled by a cooling water circulator (EYELA, CTP-3000). A gas pressure was supplied into the cell from a gas cylinder up to a prescribed pressure. The bath temperature was cooled down to a temperature which gives subcooling for hydrate crystal growth. The crystal growth was observed under an optical microscope (Edmund Optics, VZM-450) and a CCD camera (Sentech, STC-MC152USB). After sufficient amount of the crystal formed, the crystals and the residual solution was separated and the cell was cooled down to ~250 K. The cell pressure was released to atmospheric pressure. Under subsequent processes, the crystals were kept at below 250 K.

The pressure and temperature of the system were measured by a pressure sensor (KEYENCE, GP-M100) and a platinum resistance thermometer (Eutech Instruments, EcoScan Temp 6), respectively. Measurement uncertainties for pressure, temperature and TBAB composition in aqueous solution are 0.3 K, 0.1 MPa and 0.006 in mass fraction, respectively.

Table S1. Formation conditions for single crystals

Gas	Xe	Kr	Ar
TBAB composition (mass fraction)	0.204	0.200	0.200
Temperature /K	285.2	286.2	286.2
Pressure /MPa	0.4	1.0	4.2
Subcooling temperature /K	~3	~3	~6

The single crystal X-ray diffraction measurements were performed by a diffractometer (Bruker, AXS CCD). The sample temperature was maintained by cold nitrogen flow at 123 K. The structure was solved and refined by SHELXTL program[S1]. All atoms except for hydrogen and rare gas molecules were refined with anisotropic thermal parameters. Hydrogen atoms in the TBA cation were automatically placed by the program. Hydrogen of atoms in water molecules were manually placed using a difference Fourier map. The measurement and refinement results are summarized in Table S2 in Supplementary Information. CCDC 1935565-1935567 report CIF data for the presently found crystal structures. The whole cage arrangements in the presently determined structures are provided in Fig. S1.

Table S2. Crystal data and structure refinement results for the TBAB + (Xe, Kr or Ar) hydrate.

	TBAB + Xe hydrate	TBAB + Kr hydrate	TBAB + Ar hydrate
empirical formula	$C_{16}H_{112}NBrO38Xe_{1.17}$	$C_{16}H_{112}NBrO_{38}Kr_{1.05}$	$C_{16}H_{112}NBrO_{38}Ar_{1.23}$
formula weight, g·mol^{-1}	1203.92	1090.77	1055.91
temperature, K	123 (2)	123 (2)	123 (2)
wavelength, Å	0.71070	0.71070	0.71070
crystal system, space group	Orthorhombic, *Pmma*	Orthorhombic, *Pmma*	Orthorhombic, *Pmma*
unit cell dimensions, Å	a = 21.088(5) b = 12.630(3) c = 12.063(3)	a = 21.064(3) b = 12.6451(19) c = 12.0298(18)	a = 21.041(3) b = 12.6523(15) c = 12.0228(14)
volume, Å^3	3212.9(12)	3204.2(8)	3200.7(7)
Z, calculated density, g·cm^{-3}	2, 1.160	2, 1.131	2, 1.096
absorption coefficient _mu	1.324	1.405	0.784
$F(000)$	1270	1180	1152
crystal size, mm	0.15 × 0.30 × 0.30	0.15 × 0.20 × 0.20	0.10 × 0.10 × 0.15
θ range for data collection	2.516, 28.275	2.337, 28.279	2.337, 28.281
index ranges	$-27 < h < 24$ $-13 < k < 16$ $-7 < l < 16$	$-28 < h < 26$ $-16 < k < 11$ $-16 < l < 13$	$-23 < h < 27$ $-16 < k < 16$ $-12 < l < 15$
reflections collected/unique	4059/ 3869	4113/ 3800	4266/ 3859
completeness to 2θ	0.949	0.964	0.978
refinement method	F^2 against all reflections	F^2 against all reflections	F^2 against all reflections
data/restraints/parameters	4059/ 61/ 387	4113/ 105/ 428	4166/ 78/ 386
goodness-of-fit on F^2	1.012	1.098	1.112
final R indices [$I > 2\Sigma(I)$] R_1, wR_2	0.0310, 0.0825	0.0417, 0.1251	0.0402, 0.1264
R indices (all data) R_1, wR_2	0.0325, 0.0846	0.0452, 0.1272	0.0427, 0.1278

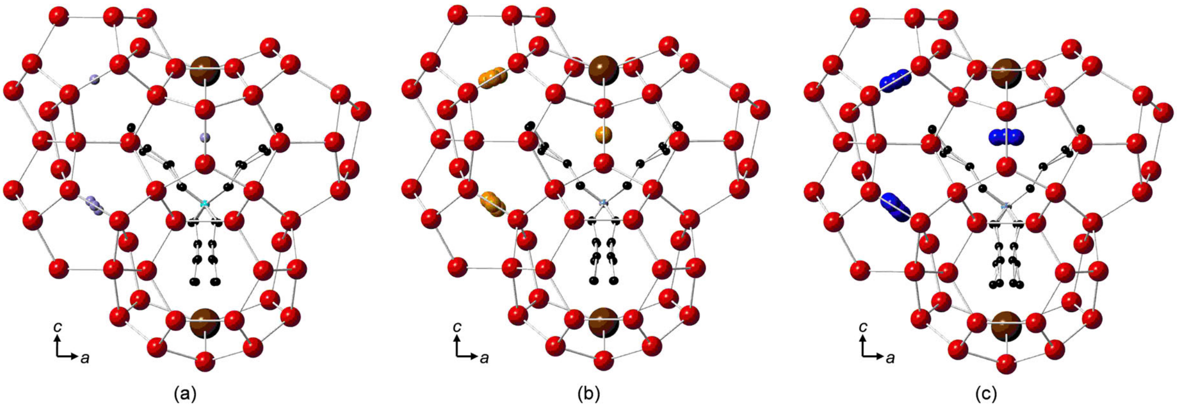

Fig. S1. Whole cage arrangements in the presently determined structure. (a) TBAB + Xe hydrate (b) TBAB + Kr hydrate (c) TBAB + Ar hydrate. Ball: Red, oxygen of water molecule; Light blue, Xe; Orange, Kr; Blue, Ar; Cyan, N; Black, C; Brown, Br.

2. Supplementary Information for D cage shapes

Fig. S2 shows the three D cages found in each of the present three structures. This figure shows the distortion of the D_{d1} cages with two indented water molecules. In the D_{d1} cage Xe and Kr stay mostly in one position, i.e., the centre of the cage. Contrary to this, the Ar has three positions (two of them are in a symmetry-related position) in the D_{d1} cage. Compared to relatively large Xe and Kr molecules, the smallest Ar molecule was able to distribute in the cage. However, the possible positions align along the *a* axis, which means that the molecular orientation in the D_{d1} cage is still restricted even with a smaller molecular size such as Ar.

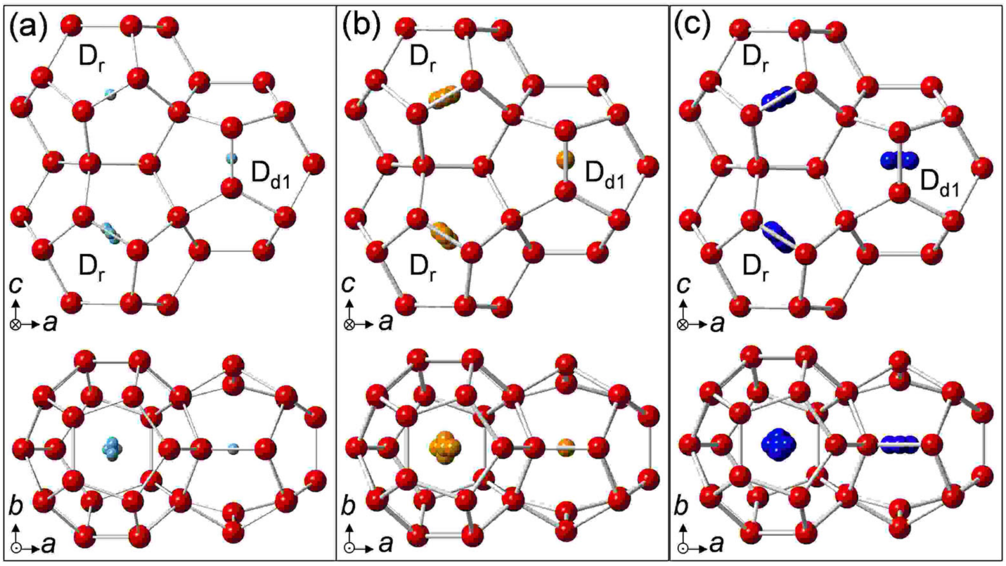

Fig. S2. Guest distributions in the D cages.. (a) TBAB + Xe hydrate (b) TBAB + Kr hydrate (c) TBAB + Ar hydrate. Ball: Red, oxygen of water molecule; Light blue, Xe; Orange, Kr; Blue, Ar. Bar: Hydrogen bond between water molecules.

Table S3 shows distances between cage center and cage water molecules in the D cages.

Table S3. Distances between cage center and cage water molecules in the D cages. D_r with "blue" and "green" denote the two different D_r cages in Fig. 4 in the context. Units are Å.

Cage	Xe	Kr	Ar
Longest distances			
D_r (blue)	4.0735	4.0172	4.0227
D_r (green)	4.0796	4.0203	4.0094
D_{d1}	4.0838	4.0274	4.0079
Shortest distances			
D_r (blue)	3.7251	3.7285	2.9856
D_r (green)	3.7088	3.7090	2.9990
D_{d1}	3.7028	3.7047	3.0121
Average distances			
D_r (blue)	3.8742	3.8625	3.8642
D_r (green)	3.8707	3.8664	3.8613
D_{d1}	3.8180	3.8153	3.8151

References in Supplementary Information

S1 G. M. Sheldrick, *Acta Crystallogr.*, 1990, **A46**, 467.