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Article

Generation of a Plastic Crystal Including Methane Rotator within Metal-Organic Cavity by Forcible Gas Adsorption

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The structural determination of saturated adsorbed methane inside a metal-organic cavity by the forcible pressure swing adsorption method (ca. 13 MPa) through a gas-adsorption equilibrium state gives a methane inclusion crystal even at 298 K. The adsorbed methane molecules regularly locate in the pocket-like narrow corners of the necks of the 1-D channel without disorder. The thermal motion of the pseudo-spherical methane molecules seems to be effectively suppressed in its translation mode but allowed rotation. In cooling to 90 K, the crystal structure remained essentially unchanged while the thermal motion decreased, indicating that a lower temperature reduces the rotation of the adsorbed pseudo-spherical methane. The observed crystal structure could also be influenced by a reduction of the vibrational magnitude, and a phase transition from a static disordered structure to an ordered state might occur. The observed crystal state at a higher temperature should have a plastic crystal nature in terms of the randomness of the orientation of incorporated guests. The single-crystal adsorbent is effective for crystallographic observation of the thermal activated guest forced into regular alignment in the crystal lattice, which can be used as a model of the supercritical fluid.

Introduction

Many metal-organic porous host solids capable of adsorbing gas have been synthesized.[1] As one important reason for doing this, the obvious application for supercritical methane storage[2] has facilitated the study of porous metal-organic adsorbents by their distinct advantage in synthetic design of a regular pore size and high porosity. However, a precise structural analysis has not yet been elucidated for only the gas adsorption state. Recently, efforts have been made for direct crystallographic characterization of the frozen inclusion solid generated at low temperature through the gas adsorption process under a powder state[3] and a single-crystal state.[4,5] However, a precise crystallographic determination for those under the adsorption equilibrium state is thought to be much more difficult because of the difficulty in realizing a high adsorption state and the vigorous activity of the adsorbed guests in thermal motion.

Recently, we found single-crystal adsorbents by the assembly of transition metal complexes, $[M(II)_2(bza)_4(pyz)]_n$ (bza and pyz = benzoate and pyrazine, M = Rh(**1**)[6] and Cu[7]), which are suitable for the study of gas-containing structures through gas adsorption. They can generate various guest inclusion crystals by transition from an empty α to an inclusion β phase through the process of smooth gas physisorption; guests are adsorbed into the generated narrow channels of the β lattice. The inclusion formation of these crystals can be controlled by the control of gas adsorption phenomena through gaseous guest pressure and temperature.[4]

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(1) (a) Mori, W.; Inoue, F.; Yoshida, K.; Nakayama, H.; Takamizawa, S.; Kishita, M. *Chem. Lett.* **1997**, *1997*, 1219. (b) Kondo, M.; Yoshitomi, T.; Seki, K.; Matsuzaka, H.; Kitagawa, S. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1725. (c) Li, H.; Eddaoudi, M.; Groy, T. L.; Yaghi, O. M. *J. Am. Chem. Soc.* **1998**, *120*, 8571.

(2) (a) Fujiwara, M.; Seki, K.; Mori, W.; Takamizawa, S. Patent Nos. JP 09132580 1995, EP 0727608 1996. (b) Seki, K.; Kitagawa, S.; Kondo, M. Patent No. JP 09227572 1997. (c) Eddaoudi M.; Kim J.; Rosi N.; Vodak D.; Wachter J.; O'Keeffe M.; Yaghi O. M. *Science* **2002**, *295*, 469.

(3) Kitaura, R.; Kitagawa, S.; Kubota, Y.; Kobayashi, T. C.; Kindo, K.; Mita, Y.; Matsuo, A.; Kobayashi, M.; Chang, H.-C.; Ozawa, T. C.; Suzuki, M.; Sakata, M.; Takata, M. *Science* **2002**, *298*, 2358.

(4) (a) Takamizawa, S.; Nakata, E.; Yokoyama, H.; Mochizuki, K.; Mori, W. *Angew. Chem., Int. Ed.* **2003**, *42*, 4331. (b) Takamizawa, S.; Nakata, E.; Saito, T. *Inorg. Chem. Commun.* **2003**, *6*, 1415.

(5) (a) Takamizawa, S.; Nakata, E.; Saito, T. *Inorg. Chem. Commun.* **2004**, *7*, 1. (b) Takamizawa, S.; Nakata, E.; Saito, T. *CrystEngComm* **2004**, *6*, 39. (c) Takamizawa, S.; Nakata, E.; Saito, T.; Akatsuka, T.; Kojim, K. *CrystEngComm* **2004**, *6*, 197.

(6) Takamizawa, S.; Hiroki, T.; Nakata, E.; Mochizuki, K.; Mori, W. *Chem. Lett.* **2002**, *2002*, 1208.

(7) Takamizawa, S.; Nakata, E.; Yokoyama, H. *Inorg. Chem. Commun.* **2003**, *6*, 763.

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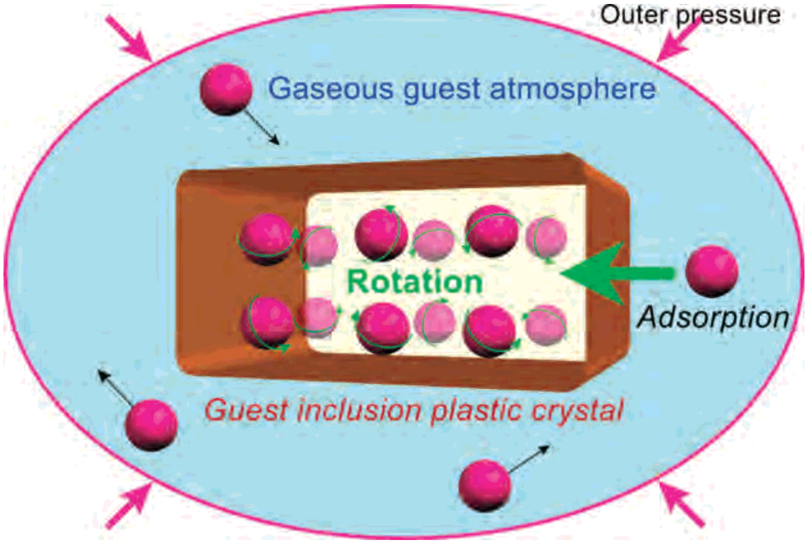
Scheme 1. Schematic Drawing of Methane Inclusion Plastic Crystal



They also exhibit a high degree of stability during the gas adsorption process and show a remarkable ability to force the alignment of light guests in metal-organic channels.[8] In this study, we attempted to ascertain the structure of adsorbed methane in the narrow cavity of **1** under a pressurized condition, which would provide essential information for better understanding the stabilization mechanism of the porosity in adsorbing supercritical gases.

Experimental Section

Single crystals of **1** were prepared by the method previously reported.[6] Gas adsorption isobar and isotherm measurements for methane (99.99% purity) were performed by a gravimetric method at 50 Torr (Cahn 2000, Cahn) and by a volumetric method at 195 K (Autosorb-1MP, Quantachrome). Single-crystal X-ray diffraction data for all structures was measured on a Bruker SMART APEX CCD area (graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) with a nitrogen flow-temperature controller. A well-formed single crystal **1** was sealed inside a thick-walled glass capillary with solid methane (2 mm length in a 12-mm long capillary) condensed in a liquid nitrogen bath. The inner pressure of the methane was approximately 13 MPa at room temperature. The measurements were carried out at 298 K and 90 K. The crystal data for **1**•2(CH_4) is given in Table 1. Empirical absorption corrections were applied using SADABS. The structure was solved by direct methods (SHELXS-97) and refined by full-matrix least-squares calculations on F^2 (SHELXL97). The non-hydrogen atoms were refined anisotropically; the hydrogen atoms except for guest methane were fixed at calculated positions. The hydrogen atoms of the methane molecules were added and refined only for the structure at 90 K because they could not be found in the crystal data of 298 K. This was most probably caused by the thermal motion of the guest methane in the crystal lattice. CCDC-260650 and 260651.

Result and Discussions

Table 1. Crystallographic Data for Single-Crystal Host **1**[a] under the Condition of Forcible Adsorption

complex	**1**•2(CH_4)	**1**•2(CH_4)
phase of environment methane	gas (ca. 13 MPa)	solid
empirical formula	$C_{34}H_{24}N_2O_8Rh_2$[b]	$C_{34}H_{32}N_2O_8Rh_2$
M	794.37	802.44
cryst syst	triclinic	triclinic
space group (number)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
T/K	298	90
a/Å	9.582(3)	9.569(3)
b/Å	10.367(4)	10.255(4)
c/Å	10.844(4)	10.738(4)
α/deg	71.594(7)	72.046(7)
β/deg	65.102(7)	64.888(7)
γ/deg	62.925(8)	62.939(7)
V/Å^3	859.7(5)	841.0(5)
Z	1	1
D_{calcd}/Mg m^{-3}	1.534	1.584
μ(Mo Kα)/mm^{-1}	1.010	1.033
reflns collected	5001	4772
independent reflns (*R*int)	3021(0.1300)	2543(0.1107)
GOF	0.906	0.957
R1 ($I > 2\sigma$ (all data))	0.0786 (0.1798)	0.0986 (0.1583)
wR2 ($I > 2\sigma$ (all data))	0.1627 (0.2282)	0.2229 (0.2618)
least diff. peak (hole)/e Å^{-3}	1.008 (−1.430)	3.104 (−3.279)

[a] Red plate; 0.30 × 0.24 × 0.06 mm^3. [b] The hydrogen atoms of the guest methane could not be located from the crystal data.

Methane Adsorption Properties. The adsorption isobar and isotherm curves of **1** for methane revealed smooth adsorption behavior with reversibility. Under a pressure of 50 Torr for the isobar measurement, methane gas adsorption begins at around −70 °C and then becomes almost saturated at ca. −120 °C with 2.0 methane molecules per Rh_2 (Figure 1a). Surprisingly, the saturation temperature is relatively higher than its condensing temperature (ca. −180 °C), which probably indicates an effective stabilization method for light guests such as methane. This ease of saturation is also observed in the isotherm measurement. A smooth adsorption ability at −78 °C, which is regarded as commonly observed in microporous media, demonstrated adsorption of 2.2 methane molecules, which is in good agreement with that in a saturated condition from isobar measurement (Figure 1b). The integer value of the saturated amount in both curves indicates that the methane molecules are held in the narrow channel with a regular arrangement. Considering the smooth gas adsorption activity of **1** for methane, the guest methane should easily pass through the narrow necks (refer to Figure

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[8] Takamizawa, S.; Nakata, E.; Saito, T. *Angew. Chem., Int. Ed.* **2004**, *43*, 1368.

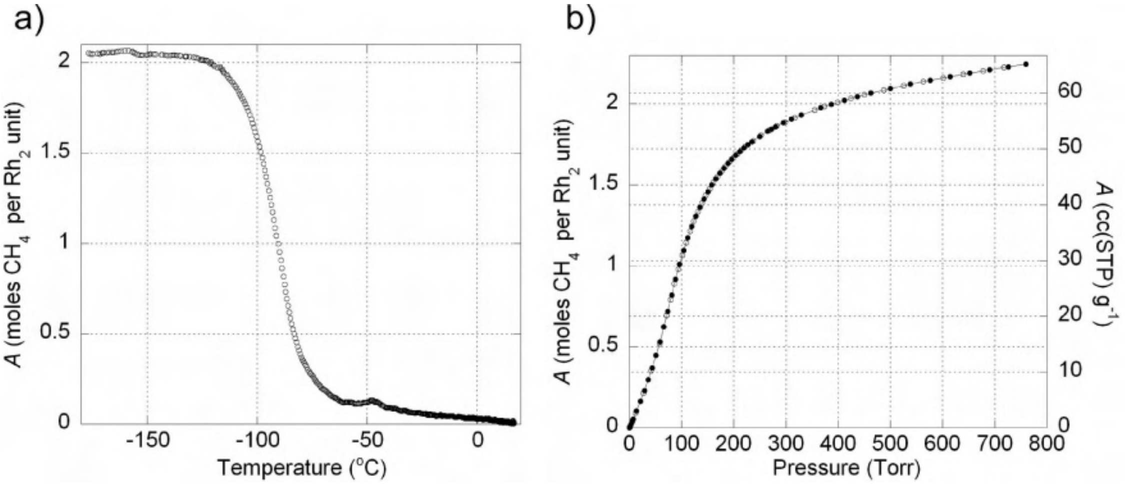

Figure 1. Methane adsorption curves for **1:** isobar at 50 Torr (a) and isotherm at −78 °C (b) (*A*: adsorbed amount of methane gas. Adsorption (solid circles), desorption (open circles)).

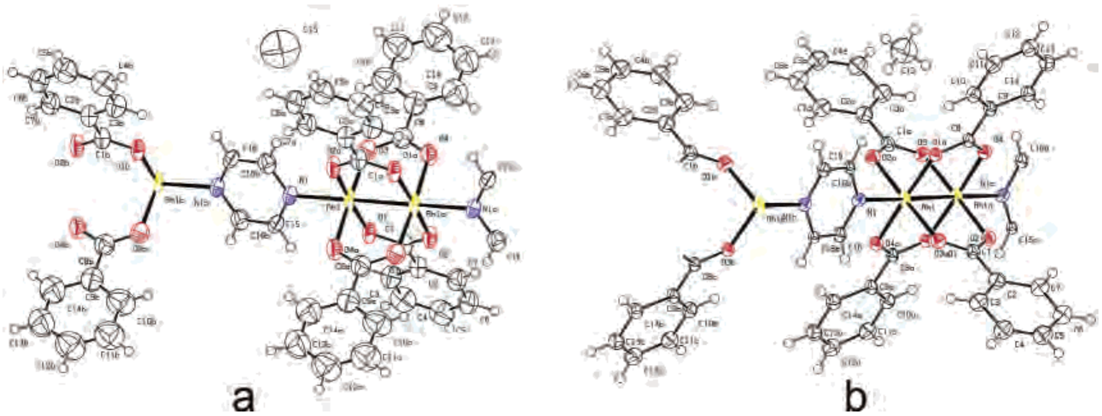

Figure 2. Thermal ellipsoid drawing of the asymmetric units at the 50% probability level with atom labeling scheme of **1**•2(CH_4) at 298 K (a) and 90 K (b). (The hydrogen atoms of the guest methane for (a) (298 K) could not be located from the crystal data.)

4a). The dynamic effect of host and guest structure to facilitate gas adsorption and stabilization of light gas are quite interesting.

Crystal Structure under Forcible Adsorption State. X-ray diffraction measurement was conducted at 298 K with pressurized methane gas of ca.13 MPa to achieve maximum gas adsorption even at room temperature. Single-crystal X-ray diffraction analysis demonstrated the generation of the saturated crystal **1**•2(CH_4) (Figures 2 and 3), which agrees well with the chemical composition determined by the adsorption measurement. The methane molecules solidified into pseudo-crystal state with full crystallographic occupation, where the two adsorbed methane molecules coherently located in a crystal period without disorder in cage-like cavities continuing with narrow necks with ca. 2 Å diameter (Figure 4a). This means that incorporating methane almost reaches the saturated adsorption state by forcible adsorption and crystallizes in terms of the molecular position, where its translation mode is most likely suppressed to the solid state rather than fluid even through maintaining adsorption equilibrium at a temperature of 298 K. However, the pseudo-spherical methane can rotate vigorously at the regular position in the crystal period. This state would be regarded as a mesophase between fluid and solid in terms of the phase of included guest.

The short contact and pertinent distances are depicted in Figure 4c and Table 2. The adsorbed methane is stabilized in the pockets at both sides of the neck by the surrounding of the corner surface. The methane molecules are captured by the π-orbital of the orthogonal conjugate planes of the benzoate moieties with atomic distances of 3.65−4.64 Å through methyl···π interaction. The methyl···H−C(benzene) semi-coordination also stabilizes by the surroundings of three benzene edges of 3.70−4.42 Å and the secondary pyrazine carbon of 4.55 Å. The adsorbed pseudo-spherical methane molecules are coherently divided into isolated pairs in each of the cavities and seem to occupy separate positions within each cavity. The separation distance of 6.499 Å is larger than the sum of van der Waals radii of C−H···H−C of 5.8 Å, which may be caused by the repulsive intermolecular force between neighbor methane molecules capable of direct contact. This is probably correlated with the thermal motion of the confined methane molecules similar to a supercritical fluid because the methane guests within the cavities are concentrated into the high density as in a condensed liquid state, and thus should have properties analogous to the supercritical phase at room temperature.

Dependence of Crystal Structure upon Temperature. Determination of the structure at 90 K was also conducted. The methane arrangement in the cavity was essentially

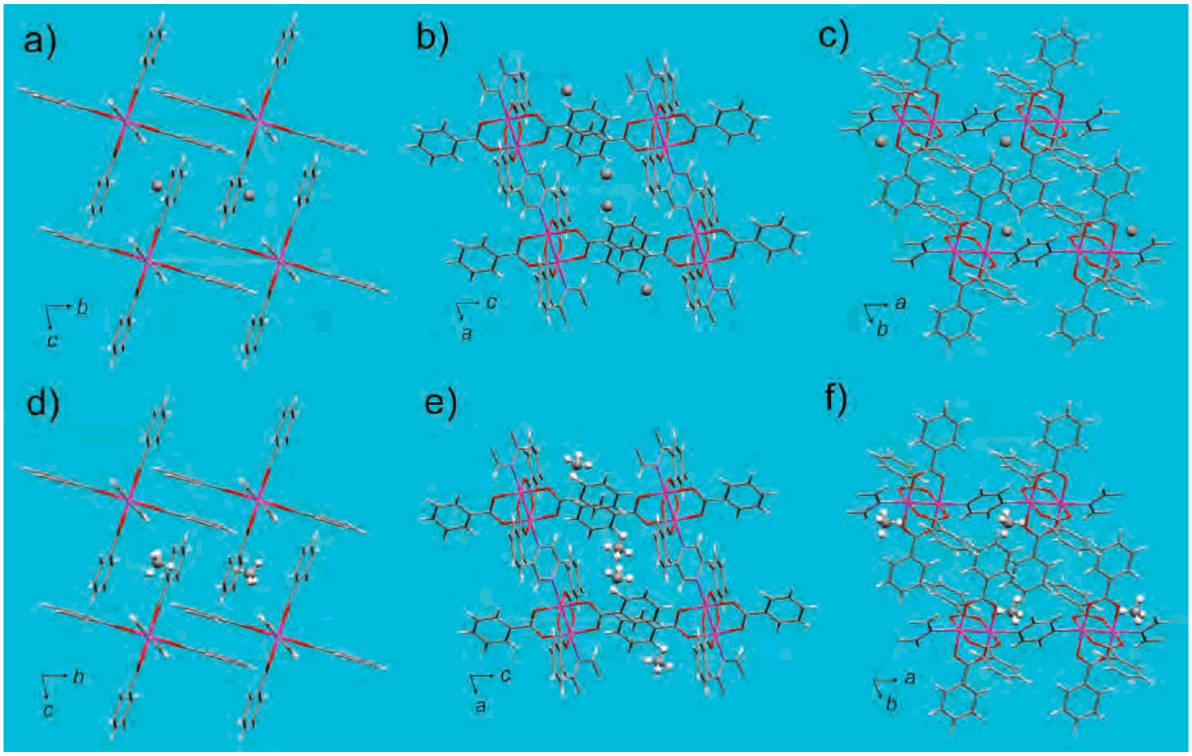

Figure 3. Packing views of crystal **1**•2(CH_4) down the *a* axis (a, d), *b* axis (b, e), and *c* axis (c, f) at 298 K (a, b, c) and 90 K (d, e, f). The adsorbed guests are represented using a ball-stick model. Elements are color-coded: rhodium (magenta), carbon (gray), hydrogen (white), nitrogen (blue), and oxygen (red).

Table 2. Atomic Distances around Methane Center in **1**•2(CH_4) (Å)[a]

	298 K	90 K
Benzoate Plane (Blue)		
C(1s)···C(1)	3.798	3.774
C(1s)···C(2)	3.841	3.809
C(1s)···C(3)	3.990	3.983
C(1s)···C(4)	4.637	4.683
C(1s)···C(7)	4.401	4.476
C(1s)···O(1)	3.951	3.826
C(1s)···O(2)	4.286	4.243
Benzoate Plane (Green)		
C(1s)···C(8)	3.673	3.538
C(1s)···C(9)	3.652	3.541
C(1s)···C(10)	3.971	3.903
C(1s)···C(14)	4.054	3.987
C(1s)···O(3)	4.187	4.108
C(1s)···O(4)	3.868	3.688
Benzene Edge (Orange)		
C(1s)···C(10)′	3.929	4.013
C(1s)···C(11)′	3.995	4.092
C(1s)···C(13)″	3.940	3.900
C(1s)···C(14)″	3.701	3.664
Benzene Edge (Yellow)		
C(1s)···C(5)′	3.834	3.820
C(1s)···C(6)′	4.424	4.353
Pyrazine		
C(1s)···C(15)′	4.552	4.545
Neighbor Methane		
C(1s)···C(1s)′ in cage	6.499	6.632
C(1s)···C(1s)″ intercage	4.807	4.490

[a] The referring atom numbers are based upon the structure at 298 K, as shown in Figure 4c.

unchanged (Figure 4a,b) although the cell volume decreased by 2.2%. However, the thermal factor of the guest methane effectively decreases (Figure 2), which seems to be a reduction of the thermal motion of the guest methane in approaching the ordinal crystal state. Furthermore, the hydrogen atoms were located from the crystal data collected at 90 K, while they could not be found in that of 298 K. These results may indicate that the decrease in temperature effectively depresses the rotation mode of the confined methane. Consequently, the atomic distances among the guests and pocket surface changed significantly (Table 2). At 90 K, the distance between the methane and benzoate planes consisting of cavity corners diminishes, which indicates the reduction in thermal motion as the temperature decrease enhances host−guest interaction. The intermolecular distance of the methane molecules in the same cavity elongated from 6.499 to 6.632 Å, which indicates the loss of intermolecular interaction within the methane pair. This result possibly provides a novel method of stabilizing ultramicropores for supercritical gases, in which the cooperative stabilization of a gas inclusion solid occurs not only by host−guest attraction but also by guest−guest repulsion, which usually works disadvantageously in condensation under the bulk state.

Conclusion

The success of a crystallographic determination of adsorbed light gas such as methane would be the first reported case. In fact, the light oxygen molecules adsorbed in the channels could not be located by single-crystal X-ray diffraction analysis by using a similar method at room temperature.[8] From the perspective of structural analysis for gas adsorption, single-crystal X-ray measurements for gas inclusion crystals can directly provide the necessary information for understanding the mechanism of gas adsorption and

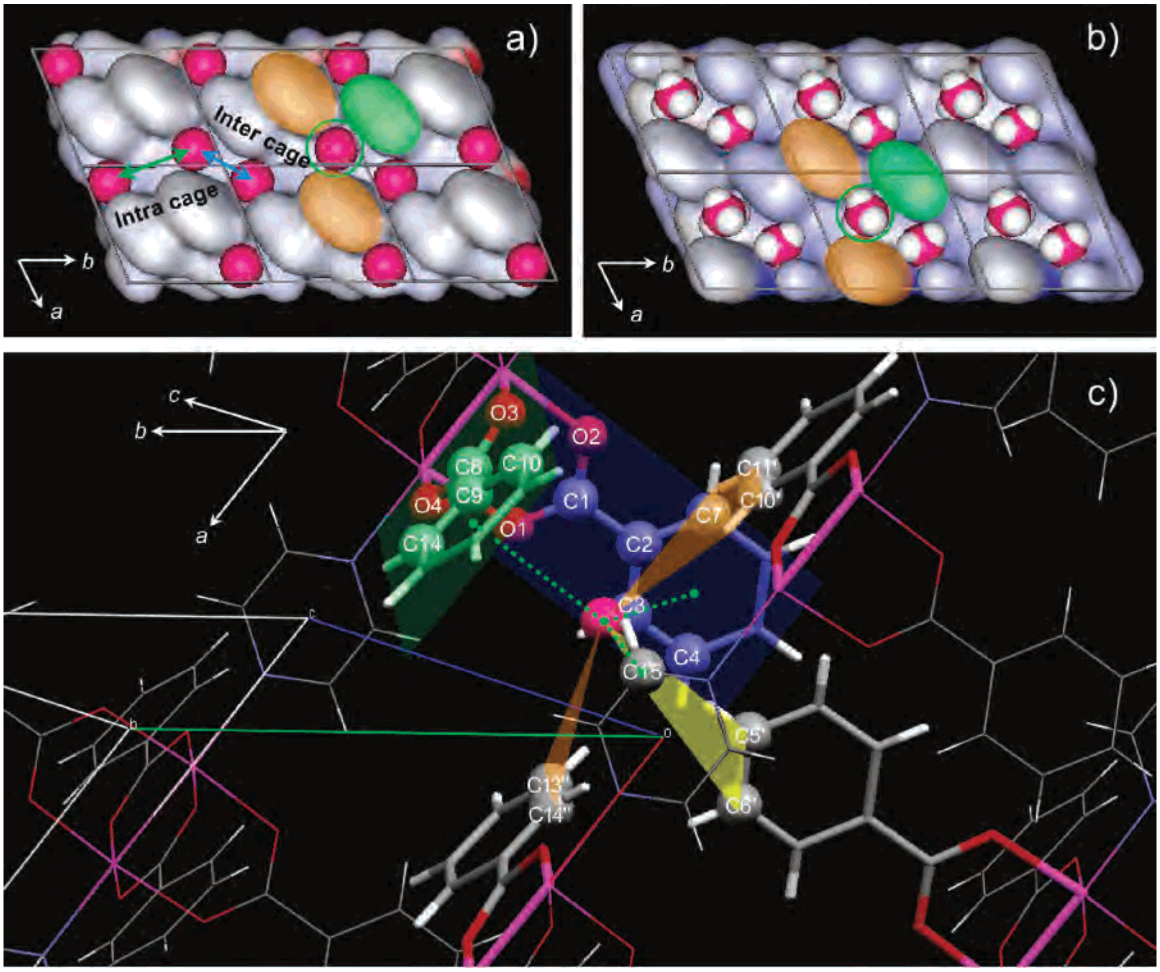

Figure 4. Surface view of channels of **1**•2(CH_4) in a space-filling model down the *c* axis at 298 K (a) and 90 K (b) and the environment of adsorbed CH_4 at 298 K with pertinent atomic distances (c). (Pink carbon indicates the guest CH_4 molecule. The contacting benzene surface and edge are colored for clarification.)

the processes for the various guests. The structures at both high and low temperatures, which are, respectively, under an adsorption equilibrium state and approaching freezing into an ordinal crystal state, are essentially unchanged. This strongly suggests that this case is an example showing the validation of the frozen structure for a discussion of the gas adsorption structure. The forcible adsorption of methane gas most likely produces a plastic crystal,[9] which can be regarded as a mesophase between the fluid and solid state of the phase of a guest incorporated in a crystal host solid in terms of the randomness of guest orientation while the molecules align regularly along the crystal period. The adsorbed methane guests are supported by the weak intermolecular force on the orthogonal planes of the benzoate moieties and benzene edges, which consist of the pocket-like narrow portions of the cavity corners. The observed crystal structure seems to indicate that the minimum potential positions of methane locate in the pocket-like narrow portions of the cavity. Furthermore, the intermolecular interaction between methane and the pocket surface seems to be forcibly strengthened by the repulsive force among the pairing methane molecules within the same cavity, which should correlate to the guest thermal motion. This indicates that the cooperative stabilization method of the gas-incorporated state occurs through the attractive force between the narrow portion of the host and guest, and the repulsive force between thermal-activated guests. Considering that the density of adsorbed methane in **1** should be similar to that of its condensed state, this indicates that the observed methane guest displays properties similar to its supercritical fluid state. Thus, the described single-crystal adsorbent is experimentally effective for crystallographic observation of thermal-activated guest forced into regular alignment in the crystal lattice. It can be used as a model of the supercritical fluid. Furthermore, the development of a method to further control molecular orientation as well as molecular alignment of included guests for crystallization will contribute to the design of a storage apparatus for light supercritical gases such as hydrogen and methane.

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Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) Meyer, R. J. *Phys. Rev. B: Solid State* **1976**, *14*, 4094.