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The Structure of the Cyclodextrin Complex. XVII. Crystal Structure of β-Cyclodextrin-Hexamethylenetetramine (1:1) Complex Hexahydrate

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The crystal structure of β-cyclodextrin–hexamethylenetetramine (1:1) complex hexahydrate was determined by the X-ray diffraction method. The crystal is monoclinic with the space group $P2_1$, $Z=2$, $a=15.285(3)$, $b=10.345(2)$, $c=20.118(2)$ Å, and $\beta=102.14(1)°$. The structure was solved by inspection of a Patterson map and the trial-and-error method combined with the rigid-body least-squares technique and refined by the block-diagonal least-squares method to the R-value of 0.056 for 4369 reflections ($\sin\theta/\lambda<0.55$). The β-cyclodextrin molecule is slightly distorted from the regular heptagonal structure. The orientation of two primary hydroxyl groups is statistically disordered. The secondary hydroxyl groups form intramolecular hydrogen bonds between adjacent glucose residues. The guest hexamethylenetetramine molecule, being located roughly at the center of the β-cyclodextrin ring, is in van der Waals contact with the interior surface of the host molecule. Two out of four nitrogen atoms of hexamethylenetetramine form N···H–O hydrogen bonds with water and adjacent β-cyclodextrin molecules. β-Cyclodextrin molecules are stacked along the crystallographic b axis, with which the plane through seven glycosidic oxygen atoms makes an angle of 46.7°, forming a "cage-type" packing. Water molecules occupy the intermolecular spaces between β-cyclodextrin molecules.

Cyclodextrins form inclusion complexes with a variety of guest molecules, of which shape and size are suitable to be accommodated within the cavity of the host macrocyclic ring.[1,2] Several β-cyclodextrin complexes with alcohol[3–5] and aromatic compounds[6–12] have been investigated by the X-ray method, and in these complexes the guest molecules have been found to be included within the host cavity. Compared with such linear or planar molecules, spherical molecules can be expected to be more favorably accommodated within the cylindrical cavity of β-cyclodextrin. Previously, we determined the crystal structure of the β-cyclodextrin-1,4-diazabicyclo[2.2.2]octane complex,[13] a complex with a spherically-shaped guest molecule. Hamilton and Sabesan have also reported the structure of the β-cyclodextrin complex with 1-adamantanecarboxylic acid[14] having a spherical adamantane moiety. In this paper, we present the crystal structure of β-cyclodextrin–hexamethylenetetramine complex in order to investigate how β-cyclodextrin includes the guest molecule with high symmetry ($\bar{4}3$ m).[15]

Experimental

β-Cyclodextrin and hexamethylenetetramine with *ca.* 1:1 molar ratio were dissolved in hot water. Colorless and prismatic crystals were obtained by standing the solution for a week at room temperature. Lattice parameters and diffraction intensities were measured on a Nicolet P3/F diffractometer with graphite-monochromated Cu $K\alpha$ radiation. The crystal was sealed in a quartz capillary with a drop of mother liquor to prevent from deterioration in air. The lattice parameters were refined by the least-squares method using 25 reflections in the 2θ range 35—40°. By using $\theta-2\theta$ scan mode, 4369 independent reflections with $|F_o|\geqq 3\sigma(F)$ were collected up to 115° in 2θ. No correction was made for absorption or extinction effect.

Crystal Data: $C_{42}H_{70}O_{35}\cdot C_6H_{12}N_4\cdot 6H_2O$, F.W.=1383.3, monoclinic, space group $P2_1$, $Z=2$, $a=15.285(3)$, $b=10.345(2)$, $c=20.118(2)$ Å, $\beta=102.14(1)°$, $V=3110.0(8)$ Å^3, $D_x=1.477$, $D_m=1.46$ g·cm^{-3}.

Determination and Refinement of the Structure

The orientation of the *pseudo* heptagonal axis of β-cyclodextrin was easily deduced by inspection of a Patterson map, and the translational parameters along the a and c axes were determined by the trial-and-error method. After the correction of the position and orientation of each glucose residue by the rigid-body least-squares method, atomic parameters were refined by the block-diagonal least-squares method. Successive Fourier and difference-Fourier syntheses revealed the positions of hexamethylenetetramine and water molecules. Occupancy factors of disordered hydroxyl groups were estimated from an electron-density map, but they were not refined. Further block-diagonal least-squares refinement of the structure, including 93 hydrogen atoms, achieved the R-value of 0.065. The quantity minimized was $\sum w(|F_o|-|F_c|)^2$ with $w=1.0$ for all the reflections. Atomic scattering factors were taken from the literature.[16] Final atomic coordinates and B_{eq} values are given in Table 1. Tables of observed and calculated structure factors, anisotropic temperature factors, atomic parameters of hydrogen atoms, bond distances, angles , and conformation angles of β-cyclodextrin, and the plane equation and atomic deviations from the plane of the seven glycosidic oxygen atoms are kept at The Chemical Society of Japan (Document No. 8440). The computation was carried out on a FACOM M-380 computer at the Center of Research Information Processing System, Agency of Industrial Science and Technology, Tsukuba.

Description and Discussion of the Structure

Outline of the Structure. A numbering scheme of the β-cyclodextrin–hexamethylenetetramine complex hexahydrate is shown in Fig. 1, and a stereo-view of the complex is given in Fig. 2. The β-cyclodextrin molecule is slightly distorted from the regular heptagonal symmetry. The guest hexamethylenetetramine

TABLE 1. ATOMIC COORDINATES AND B_{eq} VALUES

OC indicates the occupancy factor of disordered atoms.

	x	y	z	B_{eq}/Å^2	OC
C(1,G1)	6409(5)	3025(8)	1398(3)	2.87	
C(2,G1)	6555(5)	4494(8)	1459(4)	2.96	
C(3,G1)	5631(5)	5127(8)	1485(4)	3.14	
C(4,G1)	4945(5)	4721(8)	861(3)	2.79	
C(5,G1)	4876(5)	3233(8)	824(4)	3.00	
C(6,G1)	4293(6)	2835(11)	156(5)	5.75	
O(2,G1)	7218(3)	4801(6)	2049(3)	3.41	
O(3,G1)	5786(4)	6517(6)	1474(3)	4.45	
O(4,G1)	4096(3)	5232(5)	943(2)	2.50	
O(5,G1)	5760(3)	2717(5)	820(2)	2.98	
O(6,G1)	4095(4)	1461(8)	193(4)	7.23	
C(1,G2)	6866(5)	-233(8)	3465(3)	2.69	
C(2,G2)	7302(5)	1081(7)	3635(4)	2.77	
C(3,G2)	6794(4)	2085(7)	3156(3)	2.37	
C(4,G2)	6781(4)	1713(7)	2427(3)	2.20	
C(5,G2)	6407(5)	300(7)	2289(4)	2.76	
C(6,G2)	6530(5)	-242(8)	1605(3)	2.99	
O(2,G2)	7325(3)	1413(5)	4316(2)	3.04	
O(3,G2)	7235(3)	3332(5)	3263(2)	2.95	
O(4,G2)	6180(3)	2571(5)	1998(2)	2.44	
O(5,G2)	6868(3)	-576(5)	2790(2)	2.69	
O(6,G2)	7460(4)	-501(6)	1615(3)	3.52	
C(1,G3)	4220(5)	-2129(8)	4494(4)	3.62	
C(2,G3)	5053(6)	-1642(9)	4970(4)	3.75	
C(3,G3)	5520(5)	-654(8)	4606(4)	3.26	
C(4,G3)	5682(5)	-1210(8)	3952(4)	2.75	
C(5,G3)	4833(5)	-1770(8)	3506(4)	3.19	
C(6,G3)	4994(7)	-2589(11)	2921(4)	5.27	
O(2,G3)	4814(4)	-1128(7)	5557(3)	4.55	
O(3,G3)	6340(4)	-307(7)	5044(3)	4.21	
O(4,G3)	5978(3)	-177(5)	3578(2)	2.70	
O(5,G3)	4408(3)	-2646(5)	3903(3)	3.46	
O(6,G3)	5539(5)	-3693(9)	3169(5)	8.38	
C(1,G4)	926(5)	-365(8)	4377(4)	3.14	
C(2,G4)	1593(5)	-273(8)	5039(4)	3.02	
C(3,G4)	2558(5)	-204(8)	4937(3)	2.96	
C(4,G4)	2709(5)	-1305(8)	4485(4)	2.82	
C(5,G4)	2018(5)	-1314(8)	3824(4)	3.30	
C(6,G4)	2089(6)	-2465(10)	3364(4)	4.53	
O(2,G4)	1378(4)	815(6)	5414(3)	3.57	
O(3,G4)	3134(3)	-269(6)	5593(2)	3.46	
O(4,G4)	3588(3)	-1098(5)	4343(3)	3.00	
O(5,G4)	1148(3)	-1422(5)	3992(3)	3.15	
O(6,G4)	2012(7)	-3680(9)	3709(5)	9.57	0.80
O(6',G4)	1792(28)	-1985(50)	2650(23)	9.38	0.20
C(1,G5)	-760(5)	3423(7)	2819(3)	2.58	
C(2,G5)	-513(5)	3667(8)	3576(4)	2.89	
C(3,G5)	301(5)	2881(8)	3918(3)	2.82	
C(4,G5)	133(5)	1456(8)	3733(3)	2.57	
C(5,G5)	-124(5)	1279(7)	2968(4)	2.71	
C(6,G5)	-426(5)	-97(8)	2752(4)	3.44	
O(2,G5)	-327(4)	5024(5)	3709(3)	3.27	
O(3,G5)	454(4)	3073(6)	4632(2)	3.77	
O(4,G5)	958(3)	803(3)	4010(2)	2.84	
O(5,G5)	-904(3)	2088(5)	2693(2)	2.69	
O(6,G5)	-609(4)	-216(6)	2032(3)	3.78	
C(1,G6)	372(5)	6138(8)	909(4)	3.09	
C(2,G6)	29(5)	6839(7)	1478(4)	3.18	
C(3,G6)	173(5)	6003(7)	2106(4)	2.71	
C(4,G6)	-309(5)	4677(8)	1914(3)	2.65	
C(5,G6)	12(5)	4072(8)	1329(4)	3.19	
C(6,G6)	-586(6)	2917(10)	1045(4)	5.20	
O(2,G6)	519(4)	8045(5)	1610(3)	3.94	
O(3,G6)	-187(4)	6644(5)	2624(3)	3.20	
O(4,G6)	-51(3)	3892(5)	2509(2)	2.29	
O(5,G6)	-109(3)	4969(6)	759(2)	3.15	
O(6,G6)	-1565(8)	3342(14)	820(6)	5.94	0.55
O(6',G6)	-70(15)	2308(16)	559(8)	7.96	0.45
C(1,G7)	3662(5)	6138(8)	443(4)	2.84	
C(2,G7)	3393(5)	7318(8)	816(4)	3.13	
C(3,G7)	2683(5)	6943(8)	1197(4)	3.31	
C(4,G7)	1889(5)	6319(7)	714(3)	2.58	
C(5,G7)	2228(5)	5150(8)	366(3)	2.71	
C(6,G7)	1490(5)	4572(9)	-186(4)	3.82	
O(2,G7)	4182(4)	7793(6)	1260(3)	4.41	
O(3,G7)	2381(4)	8115(6)	1479(3)	4.59	
O(4,G7)	1294(3)	5905(5)	1137(2)	2.60	
O(5,G7)	2910(3)	5600(5)	19(2)	2.78	
O(6,G7)	1828(4)	3552(6)	-531(3)	4.22	
C(1,HT)	2808(8)	1224(13)	2585(6)	7.50	
C(2,HT)	4220(6)	2340(10)	2833(5)	4.59	
C(3,HT)	3059(7)	3079(13)	1952(5)	6.46	
C(4,HT)	3218(7)	2343(12)	3617(5)	5.87	
C(5,HT)	2062(7)	3108(17)	2713(7)	9.25	
C(6,HT)	3445(9)	4268(11)	2990(6)	7.20	
N(1,HT)	3496(5)	1954(9)	2284(4)	5.38	
N(2,HT)	2486(5)	1995(11)	3089(4)	6.65	
N(3,HT)	3897(5)	3114(8)	3348(4)	4.69	
N(4,HT)	2719(6)	3910(10)	2438(5)	7.47	
O(W1)	4182(7)	268(8)	1434(5)	9.48	
O(W2)	-1054(5)	833(9)	5070(4)	7.27	
O(W3)	2246(6)	956(10)	-166(6)	11.40	
O(W4)	1290(11)	204(18)	763(10)	21.86	
O(W5)	2571(5)	1725(7)	-3512(3)	5.76	
O(W6)	2014(4)	2223(6)	-2293(3)	4.10	

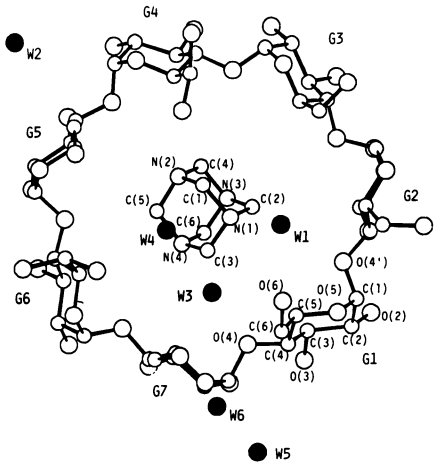

Fig. 1. Numbering scheme of the β-cyclodextrin–hexamethylenetetramine complex hexahydrate. Water molecules are shown by full circles.

molecule is located roughly at the center of the β-cyclodextrin ring, and is in van der Waals contact with the interior surface of the host molecule. β-

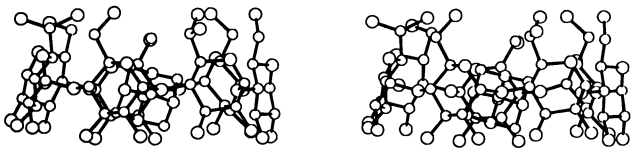

Fig. 2. Stereo-view of the β-cyclodextrin–hexamethylenetetramine complex.

Cyclodextrin molecules are stacked along the b axis, forming a "cage-type" packing. Water molecules occupy the intermolecular spaces between β-cyclodextrin molecules.

Conformation of β-Cyclodextrin. Average bond distances and angles for seven glucose residues (Fig. 3) are in good agreement with those of previously reported β-cyclodextrin complexes.[13] Two types of orientations are observed in the primary hydroxyl groups. The C(6)–O(6) bonds of the G1, G5, and G7 residues are in a *gauche-trans* conformation (to the C(5)–O(5) and C(5)–C(4) bonds, respectively), while the G2 and G3 residues have the C(6)–O(6) bonds with a *gauche-gauche* conformation. The orientation of the C(6)–O(6) bonds

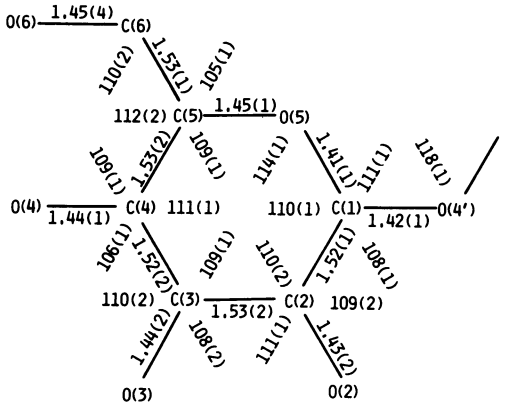

Fig. 3. Average bond distances and angles for seven glucose residues of β-cyclodextrin. Standard deviations in parentheses were estimated according to the equation:

$$\sigma = [\sum_{i=1}^{7} (x_i - \bar{x})^2/6]^{1/2}$$

where x_i refers to the bond distance or angle of the i-th residue and $\bar{x}$ is the average value.

in the G4 and G6 residues is statistically disordered, showing *gauche-trans* and *gauche-gauche* conformations.

The seven glycosidic oxygen atoms form a distorted heptagon. The radius of the heptagon, as shown in Table 2, is in the range 4.92—5.14 Å, and the O(4)···O(4′) distances between adjacent glucose residues being in the rage 4.31—4.45 Å. The average value of the radius is in good agreement with those found in the β-cyclodextrin complexes with 1,4-diazabicyclo[2.2.2]-octane (5.02 Å)[13] and 1-adamantanecarboxylic acid (5.03 and 5.08 Å).[14] The root-mean-square deviation, 0.077 Å, of O(4) atoms from the least-squares plane through the O(4) heptagon indicates the good planarity of the heptagon. As shown by the tilt-angles in Table 2, the G2, G5, and G7 residues are nearly perpendicular to the O(4) plane. The other residues incline by 14.7—17.3° with respect to the molecular axis of β-cyclodextrin, which is defined as the axis through the center of the O(4) heptagon and perpendicular to the heptagon. Distances between O(2) and O(3′) of the adjacent glucose residue are in the range 2.73—3.00 Å. These secondary hydroxyl groups are linked by the intramolecular hydrogen bonds; the O(2)-H···O(3) hydrogen bond is observed between the G1 and G2 residues, while the other hydrogen bonds are of the O(3)-H···O(2) type.

Structure of Hexamethylenetetramine. Hexamethylenetetramine has a high molecular symmetry ($\bar{4}3$ m) in the crystalline state.[15] In the cavity of β-cyclodextrin, the hexamethylenetetramine molecule shows no significant distortion from the $\bar{4}3$ m symmetry within the experimental error. The average values of C-N distance, N-C-N and C-N-C angles are 1.47(3) Å, 112(1)°, and 109(2)°, respectively. These values are in good agreement with those (1.464(4) Å, 113.3(9)°, and 107.5(5)°, respectively) found in the hexamethylenetetramine crystal at 298 K.[15]

Host-Guest Interaction. The hexamethylenetetramine molecule is roughly located at the center of the β-cyclodextrin cavity. The mirror plane through C(2,HT), C(5,HT), N(1,HT), and N(3,HT) is almost parallel to the molecular axis of β-cyclodextrin. The shortest intermolecular distance is 2.01 Å, which is found between hydrogen atoms of the C(5,HT)H_2 methylene group of the guest and the C(3,G5)H and C(5,G6)H methine groups of β-cyclodextrin. The shortest contact involving glycosidic oxygen atoms is 2.54 Å, which is found between O(4,G1) and a hydrogen atom of the C(3,HT)H_2 methylene group. The N(2) and N(4) nitrogen atoms of hexamethylenetetramine face to the interior surface of the β-cyclodextrin cavity, while the N(1) and N(3) atoms form N···H-O hydrogen bonds with the W2 water located at the primary hydroxyl side, and the O(2)-H hydroxyl group of the G3 residue in adjacent β-cyclodextrin at the secondary hydroxyl side, respectively. Therefore, the hexamethylenetetramine molecule is fixed within the β-cyclodextrin cavity by the hydrogen bonds and van der Waals force.

The position of hexamethylenetetramine in the β-cyclodextrin cavity is nearly the same as that of 1,4-

TABLE 2. GEOMETRICAL DATA FOR β-CYCLODEXTRIN

I. Radius of the O(4) heptagon

The radius is measured from the center of gravity of seven O(4) atoms to each O(4) atom.

Residue	Radius l/Å	Residue	Radius l/Å
G1	4.92	G5	5.05
G2	5.07	G6	5.07
G3	5.12	G7	5.14
G4	4.96	Average	5.05

II. O(4)···O(4) distance between adjacent glucose residues

Distance l/Å		Distance l/Å	
O(4, G1)···O(4, G2)	4.40	O(4. G4)···O(4, G5)	4.40
O(4, G1)···O(4, G7)	4.44	O(4, G5)···O(4, G6)	4.45
O(4, G2)···O(4, G3)	4.32	O(4, G6)···O(4, G7)	4.31
O(4, G3)···O(4, G4)	4.36	Average	4.38

III. Tilt-angle[a] and torsion-angle index[b]

Residue	Tilt-angle ϕ/°	Torsion-angle index ϕ/°
G1	17.3	123
G2	3.3	127
G3	16.8	120
G4	14.7	116
G5	5.3	120
G6	16.5	130
C7	6.0	119
Average	11.4	122

a) The tilt-angle is defined as an angle made by the O(4) plane and the plane through C(1), C(4), O(4), and O(4′) of each glucose residue. b) The torsion-angle index is defined as follows: $\phi = |\phi(C(1)\text{-}C(2))| + |\phi(C(2)\text{-}C(3))| - |\phi(C(3)\text{-}C(4))| - |\phi(C(4)\text{-}C(5))| + |\phi(C(5)\text{-}O(5))| + |\phi(O(5)\text{-}C(1))|$, where $\phi(C(1)\text{-}C(2))$ is the conformation angle of O(5)-C(1)-C(2)-C(3).

TABLE 3. HYDROGEN-BOND DISTANCES AND ANGLES

		Distance (l/Å)			Angle (φ/°)
		O-H	H···O	O···O	O-H···O
O(2,G1)-H·····O(3,G2)		0.85	2.03	2.87	170
O(2,G1)·····O(W6)	(f)			2.77	
O(3,G1)-H·····O(2,G7)		0.92	1.85	2.74	162
O(6,G1)···H(A)-O(W1)		0.94	1.83	2.76	170
O(6,G1)···H(B)-O(W3)		1.11	1.72	2.82	170
O(2,G2)·····H-O(3,G3)		0.93	1.99	2.92	180
O(2,G2)-H·····O(W2)	(a)	0.88	1.92	2.69	145
O(3,G2)-H·····O(3,G4)	(g)	1.14	1.78	2.87	158
O(6,G2)·····H-O(6,G5)	(a)	1.10	1.88	2.91	154
O(6,G2)·····H-O(6,G7)	(i)	1.04	2.00	2.81	133
O(6,G2)···H(B)-O(W6)	(i)	1.10	2.44	2.76	95
O(2,G3)·····H-O(3,G4)		0.96	1.78	2.73	170
O(2,G3)-H·····N(3,HT)	(j)	0.86	2.00	2.74	144
O(6,G3)·····O(W5)	(i)			2.86	
O(2,G4)·····H-O(3,G5)		0.96	2.09	3.00	158
O(2,G4)···H(B)-O(W5)	(c)	1.14	1.99	2.69	116
O(2,G4)·····H-O(2,G5)	(h)	1.05	1.72	2.75	166
O(3,G4)·····O(W5)	(c)			2.98	
O(6,G4)···H(A)-O(W2)	(h)	1.21	2.41	3.15	117
O(6',G4)·····O(2,G6)	(b)			2.54	
O(6',G4)·····H-O(3,G7)	(b)	1.21	1.75	2.69	130
O(2,G5)·····H-O(3,G6)		0.99	1.81	2.80	180
O(6,G5)·····H-O(2,G6)	(d)	0.79	2.05	2.75	148
O(2,G6)·····H-O(3,G7)		1.21	1.98	2.92	131
O(3,G6)···H(A)-O(W6)	(e)	0.69	2.29	2.80	132
O(6',G6)-H·····O(W4)		1.28	2.15	2.98	118
O(2,G7)-H·····O(W1)	(b)	1.12	2.23	2.58	95
O(3,G7)·····O(W4)	(b)			2.92	
O(6,G7)···H(A)-O(W3)		1.05	2.53	2.82	95
N(1,HT)···H(B)-O(W1)		1.13	1.93	2.80	131
O(W3)-H(A)·····O(W4)		1.05	2.47	2.72	92
O(W5)-H(A)·····O(W6)		1.15	1.68	2.81	166

Symmetry codes

None	x,	y,	z	e	$-x$,	$1/2+y$,	$-z$
a	$1+x$,	y,	z	f	$1-x$,	$1/2+y$,	$-z$
b	x,	$1+y$,	z	g	$1-x$,	$1/2+y$,	$1-z$
c	x,	y,	$1+z$	h	$-x$,	$-1/2+y$,	$1-z$
d	x,	$-1+y$,	z	i	$1-x$,	$-1/2+y$,	$-z$
				j	$1-x$,	$-1/2+y$,	$1-z$

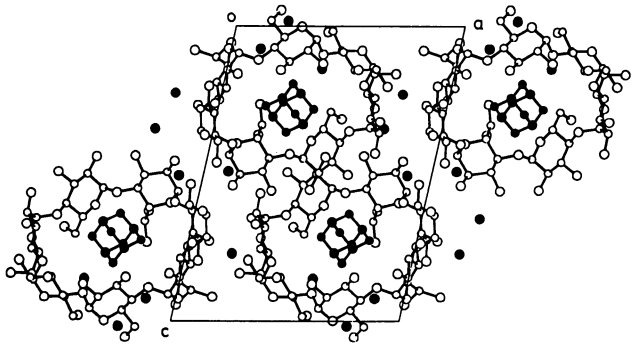

Fig. 4. Crystal structure viewed along the b axis.

diazabicyclo[2.2.2]octane,[13] but differs from that of the adamantane moiety of the 1-adamantane-carboxylic acid complex.[14] The adamantane moiety is found at the position near the primary or secondary hydroxyl side, and the carboxyl group forms hydrogen bonds with water molecules outside the cavity. Comparison of these structures suggests that the hydrogen-bond formation of the guest molecule is a more important factor to determine the host-guest geometry than van der Waals interaction.

Crystal Structure. The crystal structure is shown in Fig. 4 and 5. β-Cyclodextrin molecules are stacked along the b axis to form a "cage-type" structure similar to that found in the crystal of β-cyclodextrin.[17] The O(4) plane of β-cyclodextrin makes an angle of 46.7° with the b axis, as shown in Fig. 5. Both ends of the β-cyclodextrin cavity are blocked by adjacent β-cyclodextrin molecules. The spherical guest molecule is well accommodated within the "cage" of the β-cyclodextrin cavity. Water molecules are located in intermolecular spaces between β-cyclodextrin molecules, forming a hydrogen-bond network. W1, W3, and W4 are located near the primary hydroxyl side of the β-cyclodextrin ring, and are linked by the O(W1)-H···O(6, G1)···H-O(W3)-H···O(W4) hydrogen bonds (Table 3). W5 and W6 are also linked to each other by the O(W5)-H···O(W6) hydrogen bond, but the W2 water molecule is isolated, forming hydrogen bonds with β-cyclodextrin molecules.

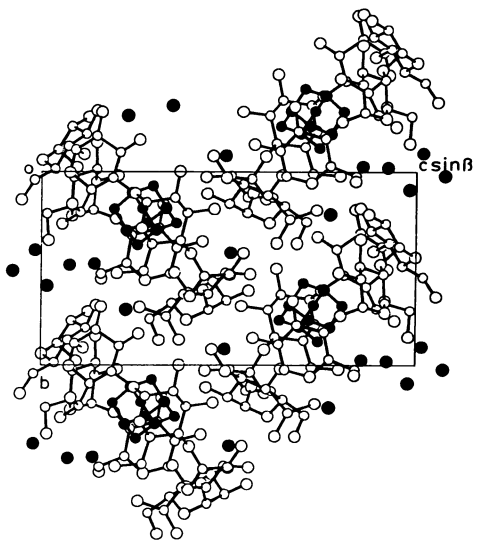

Fig. 5. Crystal structure viewed along the a axis.

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