The Structure of the Cyclodextrin Complex. VII. The Crystal Structure of the α-Cyclodextrin-DMSO-Methanol (1: 1: 2) Dihydrate Complex A Simultaneous Inclusion of DMSO and Methanol

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The crystal structure of the α-cyclodextrin(α-CDx)–DMSO–methanol (1: 1: 2) dihydrate complex was determined by the X-ray method. The crystal is monoclinic, and the space group is $P2_1$ with $Z=2$. The cell dimensions are $a=9.505(1)$, $b=14.150(1)$, $c=19.738(2)$ Å, and $\beta=102.88(1)°$. The structure was solved by an inspection of a Patterson map and by a trial-and-error method, and was refined by the block-diagonal least-squares method to the final R-value of 0.083 for 3732 reflections. The α-CDx ring is nearly hexagonal, with diagonal distances of 8.40—8.53 Å between the glycosidic oxygen atoms. The α-CDx molecules are arranged to form molecular layers perpendicular to the ac plane. The DMSO molecule is located on the secondary hydroxyl side in the α-CDx cavity, forming two hydrogen bonds with the adjacent α-CDx molecules. One methanol molecule is found on the primary hydroxyl side in the cavity, while the other is located outside the cavity. Two water molecules are distributed in the space between α-CDx molecules.

Extensive studies of inclusion and catalysis by cyclodextrins have been described.[1-3] The structure and binding force of α-cyclodextrin (α-CDx) complexes have been discussed on the basis of the structure of crystalline adducts obtained from aqueous solutions.[3-5] Recently, α-CDx was found to form complexes in a DMSO solution, and lyophobic binding has been proposed.[6] From the NMR study,[7] it seems that cyclodextrins form intramolecular O(3)–H···O(2) hydrogen bonds between the adjacent glucose residues in a DMSO solution, although the α-CDx complexes crystallized from aqueous solutions show both O(2)–H···O(3) and O(3)–H···O(2) hydrogen bonds.[4,8,9] α-CDx crystallizes from a DMSO–methanol solution. The crystal structure was determined in order to investigate the conformation of α-CDx and the α-CDx-solvent interaction in non-aqueous solutions.

Experimental

A needle-like crystal of the α-CDx–DMSO–methanol (1: 1: 2) dihydrate complex was obtained from a DMSO–methanol (1: 2) solution containing α-CDx hexahydrate (*ca.* 5%). The diffraction experiments were carried out with the crystal enclosed in a quartz capillary including a drop of mother liquor, since the crystal breaks up in air. The determination of the lattice parameters and the intensity measurement were performed on a Rigaku automatic four-circle diffractometer with graphite-monochromated Cu $K\alpha$ radiation. 3732 independent reflections with $|F_o| \geqq 3\sigma(F)$ were obtained up to 150° in 2θ by using the 2θ-ω scan technique. No corrections were made for absorption or extinction.

Crystal Data: $C_{36}H_{60}O_{30}\cdot C_2H_6OS\cdot 2CH_4O\cdot 2H_2O$, *FW* 1151.1, monoclinic, space group $P2_1$, $Z=2$, $a=9.505(1)$, $b=14.150(1)$, $c=19.738(2)$ Å, $\beta=102.88(1)°$, $V=2587.0$ Å^3, $D_m=1.46$, $D_x=1.478$ g·cm^{-3}.

Determination and Refinement of the Structure

The orientation of the α-CDx molecule in the unit cell was deduced from an inspection of a Patterson map. The position of the molecule was determined by the trial-and-error method. Then, the rigid-body least-squares technique was adopted in order to refine the position and orientation of each glucose residue. DMSO, methanol, and water molecules were found on Fourier and difference-Fourier maps. The primary hydroxyl groups of the G5 residue was found to be statistically disordered. The occupancy factors were estimated from an electron-density map, but they were not refined. Fifty-four hydrogen atoms were found on a difference-Fourier map. The refinement of atomic parameters was carried out by the block-diagonal least-squares method. The thermal factors of the hydrogen atoms were fixed as isotropic ones of the carbon or oxygen atoms to which they are bonded. The quantity minimized was $\Sigma w(|F_o|-|F_c|)^2$, with $w=1.0$ for all the reflections used. The final R-value was 0.083. The atomic scattering factors were taken from "International Tables for X-Ray

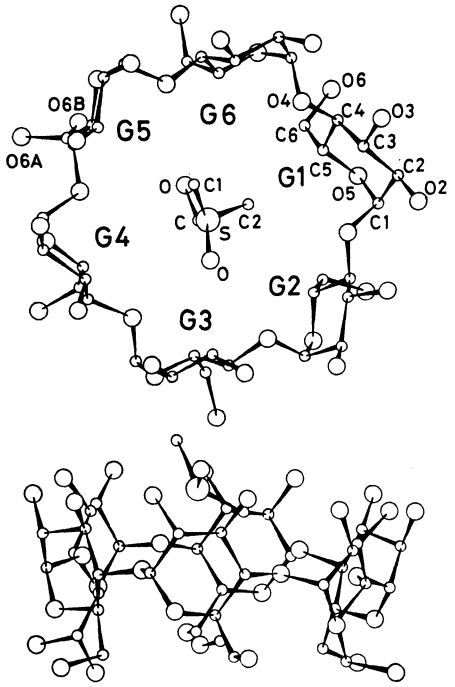

Fig. 1. Structure and numbering scheme of the α-cyclodextrin–DMSO–methanol complex.

TABLE 1. FINAL ATOMIC PARAMETERS FOR NON-HYDROGEN ATOMS ($\times 10^4$)

The anisotropic thermal factors are of the form: $\exp[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{23}kl+B_{31}lh)]$.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{23}	B_{31}
C(1,G1)	466(11)	7045(8)	342(5)	93(14)	32(6)	18(3)	52(15)	6(7)	-5(10)
C(2,G1)	-601(11)	6475(7)	650(5)	76(13)	26(5)	17(3)	-3(13)	-12(6)	-6(9)
C(3,G1)	176(12)	5938(7)	1293(5)	101(14)	24(5)	17(3)	-21(14)	6(6)	0(10)
C(4,G1)	1422(12)	5346(7)	1124(5)	133(15)	21(5)	10(2)	-4(15)	7(6)	18(10)
C(5,G1)	2400(12)	5940(8)	758(5)	122(15)	37(6)	13(3)	6(16)	1(7)	21(10)
C(6,G1)	3493(12)	5350(8)	480(6)	103(15)	36(6)	23(3)	27(16)	-3(8)	17(11)
O(2,G1)	-1651(8)	7088(6)	835(4)	91(10)	37(4)	23(2)	19(11)	-2(5)	10(8)
O(3,G1)	-790(9)	5342(6)	1533(4)	156(13)	37(4)	28(3)	-34(13)	3(6)	60(9)
O(4,G1)	2267(7)	5018(5)	1773(3)	95(9)	25(4)	15(2)	-14(10)	-1(4)	3(7)
O(5,G1)	1514(7)	6421(5)	164(3)	88(9)	30(4)	13(2)	13(10)	-1(4)	26(6)
O(6,G1)	2902(10)	4547(6)	103(4)	174(14)	37(5)	24(2)	23(14)	-8(6)	26(9)
C(1,G2)	2282(12)	10468(7)	1141(5)	125(15)	22(5)	19(3)	-16(15)	-1(7)	1(11)
C(2,G2)	778(11)	10275(8)	1172(5)	98(14)	29(5)	19(3)	-16(15)	7(7)	-2(10)
C(3,G2)	555(11)	9213(7)	1220(4)	121(15)	21(5)	9(2)	7(14)	-5(5)	9(9)
C(4,G2)	1114(11)	8698(7)	669(5)	87(13)	19(5)	13(2)	16(13)	1(6)	2(9)
C(5,G2)	2624(11)	9004(7)	608(6)	91(14)	24(5)	25(3)	-11(15)	-2(7)	-6(11)
C(6,G2)	3031(13)	8632(9)	-46(6)	128(17)	45(7)	28(4)	-15(19)	-22(9)	68(13)
O(2,G2)	372(8)	10761(6)	1741(4)	116(11)	35(4)	25(2)	26(12)	-21(5)	-3(8)
O(3,G2)	-945(8)	9019(5)	1176(4)	99(10)	35(4)	21(2)	-21(11)	-7(5)	12(7)
O(4,G2)	1147(7)	7711(5)	844(3)	103(10)	22(3)	8(2)	-19(10)	-5(4)	-3(6)
O(5,G2)	2664(7)	10020(5)	567(3)	97(9)	27(4)	17(2)	-15(10)	4(4)	12(7)
O(6,G2)	1974(11)	8807(7)	-654(4)	245(17)	55(6)	17(2)	1(17)	-3(6)	43(10)
C(1,G3)	6761(11)	10819(7)	3328(5)	75(12)	24(5)	18(3)	1(13)	9(6)	10(9)
C(2,G3)	5247(12)	11151(8)	3418(5)	120(16)	38(6)	12(3)	32(16)	12(7)	-4(10)
C(3,G3)	4081(11)	10655(8)	2939(5)	75(13)	37(6)	18(3)	15(15)	7(7)	2(9)
C(4,G3)	4235(12)	10783(7)	2178(5)	127(16)	27(5)	11(2)	-7(15)	-8(6)	2(10)
C(5,G3)	5782(12)	10545(7)	2099(5)	97(14)	27(5)	20(3)	4(15)	11(6)	-20(10)
C(6,G3)	6079(14)	10839(10)	1421(5)	156(19)	64(8)	13(3)	20(21)	-12(8)	-2(11)
O(2,G3)	5246(9)	10989(6)	4139(3)	154(13)	56(5)	10(2)	34(13)	2(5)	15(7)
O(3,G3)	2727(8)	11034(6)	2988(4)	100(11)	57(5)	26(2)	36(13)	24(6)	29(8)
O(4,G3)	3224(7)	10154(5)	1773(3)	97(10)	27(4)	17(2)	-16(10)	7(4)	-24(7)
O(5,G3)	6807(7)	11008(5)	2624(3)	77(9)	45(4)	14(2)	-17(11)	9(5)	5(6)
O(6,G3)	5719(9)	11790(6)	1246(4)	171(14)	48(5)	13(2)	-64(14)	7(5)	-9(8)
C(1,G4)	9463(11)	7811(8)	4581(5)	88(14)	44(6)	11(2)	2(15)	1(7)	10(9)
C(2,G4)	8881(10)	8577(7)	5011(5)	71(12)	33(5)	12(2)	5(13)	-1(6)	3(9)
C(3,G4)	7692(10)	9138(8)	4561(5)	63(12)	46(6)	13(2)	38(14)	13(7)	23(9)
C(4,G4)	8210(9)	9525(7)	3920(4)	46(11)	31(5)	13(2)	-17(13)	9(6)	-5(8)
C(5,G4)	8852(11)	8748(8)	3540(5)	86(13)	40(6)	16(3)	-5(15)	5(7)	28(10)
C(6,G4)	9637(12)	9132(10)	2994(6)	120(17)	64(8)	21(3)	22(20)	22(9)	57(12)
O(2,G4)	8424(8)	8094(6)	5565(3)	124(11)	48(5)	14(2)	45(12)	8(5)	26(7)
O(3,G4)	7400(9)	9901(6)	4976(4)	162(13)	43(5)	14(2)	59(13)	-9(5)	17(8)
O(4,G4)	6905(7)	9846(5)	3448(3)	69(8)	32(4)	14(2)	-24(9)	4(4)	-4(6)
O(5,G4)	9953(7)	8249(5)	4035(4)	60(8)	35(4)	20(2)	5(10)	8(5)	16(6)
O(6,G4)	10889(10)	9648(8)	3322(6)	160(15)	73(7)	54(4)	-56(18)	20(9)	101(13)
C(1,G5)	7112(12)	4430(7)	3973(5)	108(15)	27(5)	18(3)	-5(15)	-10(6)	-5(10)
C(2,G5)	7098(11)	4788(8)	4704(5)	93(14)	38(6)	16(3)	24(15)	10(7)	-10(10)
C(3,G5)	7197(11)	5883(8)	4693(5)	86(13)	43(6)	14(3)	-36(15)	-1(7)	19(9)
C(4,G5)	8474(10)	6194(7)	4415(5)	66(12)	28(5)	17(3)	-18(13)	-5(6)	0(9)
C(5,G5)	8480(11)	5731(8)	3712(5)	81(13)	44(6)	15(3)	-29(15)	-7(7)	0(9)
C(6,G5)	9957(15)	5927(10)	3517(7)	165(21)	64(9)	38(5)	-102(23)	-57(11)	106(16)
O(2,G5)	5766(8)	4501(6)	4864(4)	125(11)	54(5)	20(2)	-37(13)	8(6)	37(8)
O(3,G5)	7268(8)	6214(6)	5381(3)	132(11)	48(5)	15(2)	-47(12)	-19(5)	45(8)
O(4,G5)	8269(7)	7209(5)	4321(3)	47(8)	32(4)	18(2)	3(9)	3(4)	12(6)
O(5,G5)	8403(7)	4710(5)	3790(3)	75(9)	41(4)	17(2)	1(10)	-10(5)	21(7)
O(6A,G5)	11182(23)	5955(19)	3897(13)	44(27)	56(17)	26(8)	-28(36)	26(19)	-5(23)
O(6B,G5)	10030(15)	5524(10)	2906(7)	167(20)	65(9)	37(5)	-17(23)	7(11)	97(16)
C(1,G6)	2651(10)	4046(7)	1836(5)	72(12)	23(5)	16(3)	-10(13)	1(6)	2(9)
C(2,G6)	2443(11)	3711(8)	2553(5)	90(13)	37(6)	11(2)	-18(15)	-5(6)	8(9)
C(3,G6)	3499(13)	4247(8)	3112(5)	142(17)	38(6)	10(2)	-13(16)	1(6)	37(10)
C(4,G6)	5043(11)	4151(7)	3018(5)	96(14)	25(5)	12(2)	0(14)	9(6)	7(9)
C(5,G6)	5129(11)	4405(8)	2281(4)	99(14)	48(6)	6(2)	-32(16)	5(6)	23(9)
C(6,G6)	6631(12)	4133(10)	2128(6)	83(14)	67(8)	22(3)	17(18)	-8(9)	39(11)
O(2,G6)	1030(8)	3839(6)	2636(4)	89(10)	52(5)	27(2)	-46(12)	-9(6)	-25(8)
O(3,G6)	3436(9)	3870(7)	3784(3)	177(13)	67(6)	10(2)	-98(16)	-7(6)	28(8)
O(4,G6)	5895(7)	4775(5)	3502(3)	82(9)	20(3)	15(2)	-9(9)	0(4)	-6(6)
O(5,G6)	4074(7)	3903(5)	1782(3)	100(9)	34(4)	12(2)	2(10)	-14(4)	15(6)
O(6,G6)	6864(10)	3124(7)	2233(5)	161(14)	57(6)	35(3)	53(16)	-26(7)	2(11)
S(1,DS)	3821(12)	7756(–)	3670(3)	875(31)	62(3)	54(2)	-14(17)	-4(5)	89(14)
C(1,DS)	3519(25)	7052(18)	4425(13)	295(41)	126(19)	100(12)	95(47)	139(26)	127(37)
C(2,DS)	3029(34)	7317(26)	2896(13)	511(72)	227(35)	54(9)	-80(86)	-34(31)	-38(41)
O(1,DS)	3359(11)	8678(8)	8350(5)	204(17)	76(7)	43(4)	-48(20)	-42(9)	34(13)
C(1,M1)	126(16)	6895(12)	6767(9)	140(22)	72(11)	57(7)	0(25)	5(14)	89(20)
O(1,M1)	1022(11)	7647(8)	6632(5)	144(15)	86(8)	40(3)	37(18)	24(9)	18(11)
C(1,M2)	6107(25)	7534(20)	1769(15)	271(42)	132(21)	120(15)	94(51)	21(31)	168(42)
O(1,M2)	6726(23)	6739(15)	1921(11)	561(48)	194(20)	131(11)	255(54)	173(26)	402(41)
O(W1)	6671(11)	7601(7)	9644(5)	199(17)	55(6)	42(4)	13(17)	-3(8)	-59(13)
O(W2)	333(13)	7634(8)	8436(6)	265(22)	49(6)	58(5)	-40(20)	20(9)	-46(16)

Crystallography."[10] The atomic parameters are listed in Tables 1 and 2,* while the observed and calculated structure factors are given in Table 3.*

Description and Discussion of the Structure

Structure of α-CDx. The structure and numbering scheme of α-CDx are shown in Fig. 1. The bond distances, angles, and conformation angles are given in Tables 4—6.* The geometrical data for the α-CDx ring are shown in Tables 7 and 8. The average bond distances and angles are in good agreement with those found in other α-CDx complexes.[5,8,9,11-21] The primary hydroxyl group of the G5 residue is statistically disordered. The occupancy factors are 0.3 for O(6A, G5) and 0.7 for O(6B, G5). The C(6)–O(6A) and C(6)–O(6B) bonds show *gauche-gauche* and *gauche-trans* conformations respectively. The other primary hydroxyl groups are in the *gauche-gauche* conformation. The C(6)–O(6A) and C(6)–O(6B) bonds are significantly short, but a similar shortening of the disordered C–O bond has been observed in α-L-sorbose[22] and α-CDx complexes with Methyl Orange[12] and *m*-nitrophenol.[15]

The six glycosidic oxygen atoms form a nearly regular hexagon. The diagonal O(4)···O(4) distances of the α-CDx ring deviate 0.08 Å at most from their average value of 8.47 Å. These six O(4) atoms are coplanar within 0.14 Å. The average O(4)···O(4) distance between the adjacent glucose residues is 4.24 Å, with a maximum deviation of 0.05 Å. The symmetrical α-CDx ring has been also found in the sodium 1-propanesulfonate complex,[14] but the torsion-angle index[23] indicates that the conformation of pyranose rings changes slightly. The torsion-angle indices (128—136°) are significantly larger than those found in the sodium 1-propanesulfonate complex (126.6—128.5°).

Intramolecular O(2)···O(3) hydrogen bonds are observed between the adjacent glucose residues (Table 7). From the NMR spectra of cyclodextrins in a DMSO solution, only the O(3)–H···O(2) hydrogen bond has been suggested.[7] In the DMSO–methanol complex there are four O(3)–H···O(2) hydrogen bonds, but a O(2)–H···O(3) hydrogen bond is also observed between the G1 and G2 residues. The O(2)···O(3) distance between the G1 and G6 residues (3.25 Å) is too large for the hydrogen bond.

Table 5. Average bond distances and angles for the glucose residue

The standard deviations were estimated according to $\sigma=[\sum_{i=1}^{6}(x_i-\bar{x})^2/5]^{1/2}$, where x_i referes to the bond distances or angles in the i-th residue and $\bar{x}$ is the average value. A prime indicates the atom in the adjacent glucose residue.

I. Bond distances (l/Å)			
C(1)–C(2)	1.53(3)	C(3)–O(3)	1.42(1)
C(1)–O(5)	1.41(1)	C(4)–C(5)	1.54(1)
C(1)–O(4′)	1.42(1)	C(4)–O(4)	1.43(2)
C(2)–C(3)	1.51(3)	C(5)–C(6)	1.53(3)
C(2)–O(3)	1.43(2)	C(5)–O(5)	1.44(2)
C(3)–C(4)	1.53(2)	C(6)–O(6)	1.40(5)
II. Bond angles (ϕ/°)			
C(2)–C(1)–O(5)	110(2)	C(3)–C(4)–C(5)	112(1)
C(2)–C(1)–O(4′)	108(2)	C(3)–C(4)–O(4)	106(1)
O(5)–C(1)–O(4′)	111(1)	C(5)–C(4)–O(4)	109(1)
C(1)–C(2)–C(3)	110(2)	C(4)–C(5)–C(6)	113(2)
C(1)–C(2)–O(2)	109(3)	C(4)–C(5)–O(5)	110(1)
C(3)–C(2)–O(2)	111(2)	C(6)–C(5)–O(5)	106(1)
C(2)–C(3)–C(4)	111(1)	C(5)–C(6)–O(6)	113(3)
C(2)–C(3)–O(3)	109(2)	C(4)–O(4)–C(1′)	119(1)
C(4)–C(3)–O(3)	110(2)	C(1)–O(5)–C(5)	114(2)

* Tables 2—4 and 6 are kept at the office of the Chemical Society of Japan (Document No. 7818).

Table 7. Geometrical data for the α-cyclodextrin ring[a]

I. O(4)···O(4) distances (l/Å)			
O(4, G1)···O(4, G2)	4.26(1)		
O(4, G1)···O(4, G6)	4.29(1)		
O(4, G2)···O(4, G3)	4.19(1)		
O(4, G3)···O(4, G4)	4.27(1)		
O(4, G4)···O(4, G5)	4.19(1)		
O(4, G5)···O(4, G6)	4.24(1)		
O(4, G1)···O(4, G4)	8.40(1)		
O(4, G2)···O(4, G5)	8.53(1)		
O(4, G3)···O(4, G6)	8.49(1)		
II. Torsion-angle index (ϕ/°)			
G1 residue	133	G4 residue	130
G2 residue	133	G5 residue	136
G3 residue	134	G6 residue	128
III. Intramolecular hydrogen bonds (l/Å)			
		H···O	O···O
O(2, G1)–H···O(3, G2)		2.27(13)	2.86(1)
O(3, G3)–H···O(2, G2)		2.34(13)	2.96(1)
O(3, G4)–H···O(2, G3)		1.97(13)	2.79(1)
O(3, G5)–H···O(2, G4)		1.88(13)	2.87(1)
O(3, G6)–H···O(2, G5)		1.93(13)	2.85(1)

a) Estimated standard deviations are shown in parentheses.

Table 8. Least-squares planes and deviations of atoms (l/Å)

The plane equation is of the $AX+BY+CZ=D$ form, where X, Y, and Z are the coordinates in Å along the a, b, and c* axes respectively.

I. The plane through six O(4) atoms.

$0.772X-0.105Y-0.627Z=-1.756$

O(4, G1)	−0.06	O(4, G4)	0.03
O(4, G2)	0.14	O(4, G5)	0.07
O(4, G3)	−0.13	O(4, G6)	−0.04

II. Deviations of atoms from the plane through C(2), C(3), C(5), and O(5).

Residue	C(1)	C(2)	C(3)	C(4)	C(5)	O(5)
G1	0.69	0.01	−0.01	−0.63	0.01	−0.01
G2	0.66	0.02	−0.02	−0.58	0.02	−0.02
G3	0.70	0.01	−0.01	−0.62	0.01	−0.01
G4	0.68	0.01	−0.01	−0.65	0.01	−0.01
G5	0.71	0.02	−0.02	−0.65	0.02	−0.02
G6	0.68	0.00	−0.00	−0.64	0.00	−0.00

Table 9. Bond distances and angles in DMSO and methanol[a)]

I. Bond distances (l/Å)	
S(1, DS)–C(1, DS)	1.87(3)
S(1, DS)–C(2, DS)	1.67(3)
S(1, DS)–O(1, DS)	1.45(1)
C(1, M1)–O(1, M1)	1.43(2)
C(1, M2)–O(1, M2)	1.27(3)
II. Bond angles (ϕ/°)	
C(1, DS)–S(1, DS)–C(2, DS)	115(1)
C(1, DS)–S(1, DS)–O(1, DS)	100(1)
C(2, DS)–S(1, DS)–O(1, DS)	118(1)

a) Estimated standard deviations are shown in parentheses.

Table 10. Intermolecular distances between α-cyclodextrin and included molecules[a)]

I. α-Cyclodextrin···DMSO (l/Å)	
O(2, G3)–O(1, DS)	3.71(1)
O(3, G3)–O(1, DS)	3.73(1)
C(3, G3)–O(1, DS)	3.47(2)
O(4, G4)–O(1, DS)	3.99(1)
O(3, G5)–C(1, DS)	3.83(3)
C(3, G5)–C(1, DS)	3.80(3)
O(4, G1)–C(2, DS)	3.19(3)
II. α-Cyclodextrin···methanol (l/Å)	
C(5, G5)–O(1, M2)	3.83(2)
C(6, G6)–O(1, M2)	3.71(2)
O(6B, G5)–O(1, M2)	3.73(3)
C(5, G6)–O(1, M2)	3.77(2)

a) Estimated standard deviations are shown in parentheses.

α-CDx-Guest Interaction. The bond distances and angles in DMSO and methanol are given in Table 9. The S(1, DS)–C(1, DS) bond is longer by 0.2 Å than the S(1, DS)–C(2, DS) bond. A similar inequality of the S–C bonds has been observed in the crystal structure of DMSO.[24)] The S–O bond is shorter by 0.09 Å than that found in the crystalline DMSO. The C–O bond of M2 is shorter by 0.16 Å than that of M1. This may be due to the large thermal motion as has been found in the α-CDx–methanol complex.[8)]

The intermolecular distances between α-CDx and included guests are shown in Table 10. The sulfur atom is located at the center of the circle composed of the twelve secondary hydroxyl groups. The C(2, DS) methyl group is inserted into the α-CDx cavity, while the C(1, DS) methyl group protrudes from the cavity. The shortest contact of DMSO with α-CDx is that of 3.47 Å found between O(1, DS) and C(3, G3), suggesting van der Waals contact. The M2 methanol is located nearly parallel to the O(4) plane on the primary hydroxyl side of the cavity. In the α-CDx–methanol complex,[8)] the methanol molecule is found in a similar position, being hydrogen-bonded to the primary hydroxyl group with the *gauche-trans* conformation. In the DMSO–methanol complex, C(6, G5)–O(6B, G5) bond is in the *gauche-trans* conformation, but the O(6B, G5)···O(1, M2) distance of 3.73 Å is too large for the hydrogen bond.

Table 11. Intermolecular distances less than 3.0 Å (l/Å)[a)]

O(6, G4)–O(1, DS)	(a)	2.72
O(6B, G5)–O(2, G6)	(a)	2.66
O(2, G4)–O(1, M1)	(a)	2.93
O(6, G3)–O(6, G6)	(b)	2.76
O(2, G1)–O(1, M2)	(c)	2.95
O(3, G3)–O(6, G4)	(c)	2.80
O(3, G1)–O(6B, G5)	(c)	2.66
O(6, G2)–O(W2)	(d)	2.68
O(2, G1)–O(W1)	(e)	2.63
O(2, G2)–O(W2)	(f)	2.74
O(3, G1)–O(6, G2)	(g)	2.85
O(6, G1)–O(3, G2)	(g)	2.88
O(6, G3)–O(W1)	(h)	2.79
O(2, G3)–O(3, G5)	(h)	2.78
O(2, G4)–O(3, G6)	(h)	2.64
O(2, G6)–O(W2)	(i)	2.80
O(6, G6)–O(1, M1)	(j)	2.74
O(2, G5)–O(1, DS)	(j)	2.75
O(6, G1)–O(W1)	(j)	2.81
O(3, G4)–O(6A, G5)	(k)	2.80

Code	Symmetry code		
a	$1+x$,	y,	z
b	x,	$1+y$,	z
c	$-1+x$,	y,	z
d	x,	y,	$-1+z$
e	$-1+x$,	y,	$-1+z$
f	$-x$,	$1/2+y$,	$1-z$
g	$-x$,	$-1/2+y$,	$-z$
h	$1-x$,	$1/2+y$,	$1-z$
i	$-x$,	$-1/2+y$,	$1-z$
j	$1-x$,	$-1/2+y$,	$1-z$
k	$2-x$,	$1/2+y$,	$1-z$

a) Estimated standard deviations are in the range from 0.01 to 0.03 Å.

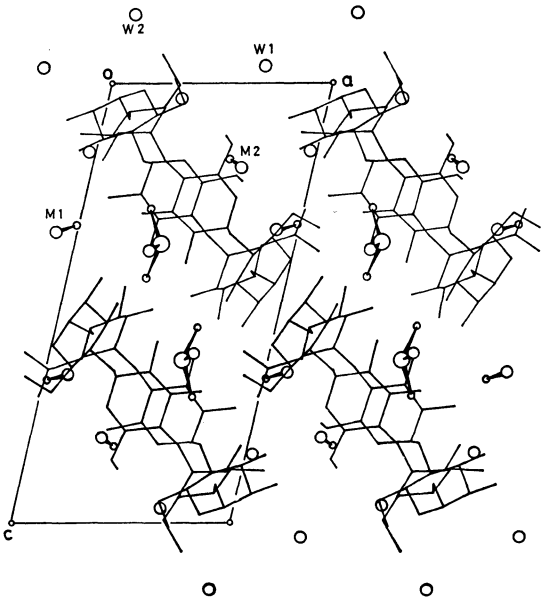

Fig. 2. The crystal structure projected on the ac plane. Circles indicate atoms in DMSO, methanol, and water molecules.

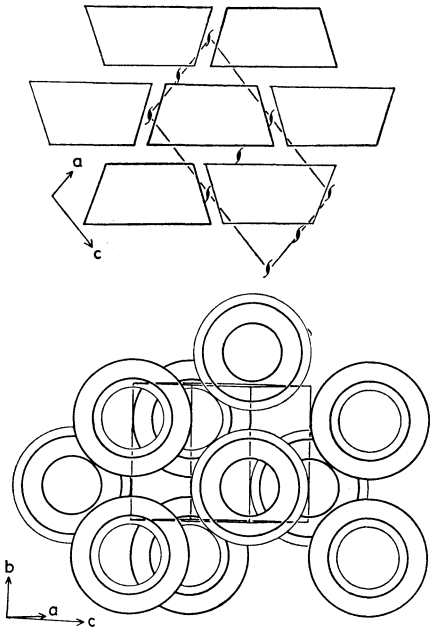

Fig. 3. A schematic drawing of the packing of α-cyclodextrin molecules.

Crystal Structure and Hydrogen Bonds. The crystal structure is shown in Fig. 2. The packing scheme of α-CDx molecules is illustrated in Fig. 3. The α-CDx molecules are arranged to form molecular layers parallel to the $(10\bar{2})$ plane. The α-CDx cavity is not connected to that of the next layer, but both ends of the cavity are open to the space between the α-CDx rings in the next layer. A similar packing of α-CDx molecules has been observed in the α-CDx complexes with *para*-disubstituted benzenes. Adjacent α-CDx molecules are linked by hydrogen bonds. In a layer, O(6, G3)–O(6, G6) (b), O(3, G1)–O(6, G2) (g), O(6, G1)–O(3, G2) (g), and O(3, G4)–O(6A, G5) (k) hydrogen bonds are observed. The adjacent layers are connected by O(6B, G5)–O(2, G6) (a), O(3, G3)–O(6, G4) (c), O(3, G1)–O(6B, G5) (c), O(2, G3)–O(3, G5) (h), and O(2, G4)–O(3, G6) (h) hydrogen bonds.

The DMSO molecule forms two hydrogen bonds with O(6, G4) (a) and O(2, G5) (j) in the next layer. The O(2)–H···DMSO hydrogen bond has also been proposed from the NMR study.[7] The methanol molecule (M2) in the α-CDx cavity is hydrogen-bonded to O(2, G1) (c), while the other methanol molecule (M1) forms two hydrogen bonds with O(2, G4) (a) and O(6, G6) (j). Thus, the DMSO and M2 methanol molecules are strongly bound to the α-CDx molecules in the next layer, although the interaction with the host α-CDx molecule seems to be weak. Each water molecule forms three hydrogen bonds with hydroxyl groups of α-CDx; O(W1) is linked to O(2, G1) (e), O(6, G3) (h) and O(6, G1) (j), while O(W2) is linked to O(6, G2) (d), O(2, G2) (f), and O(2, G6) (i).

From the DMSO methanol solution, a different crystal, which is more unstable, was obtained. The cell dimensions are $a=14.298$, $b=12.305$, $c=15.828$ Å, and $\beta=113.59°$, and the space group is $P2_1$. β-CDx crystallizes in an orthorhombic form; $a=11.428$, $b=15.549$, $c=40.025$ Å, and the space group is $P2_12_12_1$. We are attempting to elucidate these structures in order to investigate the conformation of cyclodextrins in non-aqueous solutions.

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