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Crystal structure of β-cyclodextrin–dimethylsulfoxide inclusion complex

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Abstract

β-Cyclodextrin (β-CD) crystallizes from 27% DMSO–water as β-CD·0.5DMSO·7.35H_2O in the monoclinic space group $P2_1$ with unit cell constants: $a = 15.155(1)$, $b = 10.285(1)$, $c = 20.906(1)$ Å, $\beta = 109.86(1)°$. Anisotropic refinement of 888 atomic parameters against 9,127 X-ray diffraction data converged at an R-factor of 0.055. The β-CD macrocycle adopts a 'round' conformation stabilized by intramolecular, interglucose O-3(n)···O-2($n+1$) hydrogen bonds. In the β-CD cavity, DMSO, water sites W-1, W-3 (occupancies 0.5, 0.25, 0.75) are not located concurrently with the water site W-2 because the interatomic distances to W-2 are too short (1.56–1.75 Å). DMSO is placed in the β-CD cavity such that its S-atom is shifted from the O-4 plane center to the β-CD O-6-side ca. 0.9 Å and the C–S bond which is inclined 13.6° to the β-CD molecular axis. It is maintained in position by hydrogen bonding to water site W-3 and the O-31–H group. 7.35 water molecules are extensively disordered in 13 positions both inside (W-1–W-4) and outside (W-5–W-13) the β-CD cavity. They act as hydrogen bonding mediators contributing significantly to the stability of the crystal structure. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: β-Cyclodextrin; Dimethylsulfoxide inclusion complex; Crystal structure; X-ray analysis; Hydrogen bond

1. Introduction

Cyclodextrins (CDs) are known for their ability to form inclusion complex[1] with a variety of guest molecules of suitable size which can be embedded completely or partially in the host CD cavity. The guest molecules are usually maintained in positions in the CD cavity via non-covalent interactions, e.g., hydrogen bonds, hydrophobic, van der Waals, depending on the type of guest molecule. To elucidate the host–guest interactions in CD solution, NMR technique is the method of choice[2] and DMSO-d_6 is an aprotic solvent frequently used because it gives detailed insight into the intramolecular CD hydrogen-bond network and better resolved signals for the protons.[2] DMSO has high polarity, high dielectric constant, small size and dissolves CDs up to 35 g/100 mL at 25 °C.[3] Although an inclusion complex of α-CD–DMSO was reported by Harata in 1978,[4] the complex of β-CD with a larger molecular cavity has not been found so far. Hence it is worth verifying whether DMSO can form an inclusion complex with β-CD. In this paper, we present the crystallographic evidence for a β-CD–DMSO inclusion complex and the structural comparison with the corresponding complex of α-CD.[4]

2. Experimental

Crystallization and X-ray diffraction.—β-CD purchased from Cyclolab (Budapest/Hungary) and DMSO from Merck were used without further purification. β-CD (0.05 mol) was dissolved in 2 mL of 27% DMSO–water at rt, the solution warmed at 50 °C for 1 H and cooled down slowly. The rodlike, colorless crystals formed in a few days by slow solvent evaporation.

A single crystal of β-CD–DMSO complex with dimensions 0.5 × 0.5 × 1.0 mm was mounted in a glass capillary sealed at both ends with a drop of mother

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liquor. X-ray data collection was performed at rt with a SMART CCD diffractometer (Bruker) using graphite-monochromatized MoKα radiation ($\lambda = 0.71073$ Å) operating at 50 kV, 30 mA. A total number of 22,753 reflections were measured in the θ range 1.43–30.52° (0.7 Å resolution). Data were corrected for Lorentz, polarization, and absorption effects and merged by SADABS[5] and SHELXTL[6] to yield 11,746 unique reflections. The crystal belongs to monoclinic space group $P2_1$ (for more details, see Table 1).

Table 1

Summary of crystallographic data for β-CD·0.5DMSO·7.35H$_2$O

Chemical formula	β-CD·0.5C$_2$H$_6$SO·7.35H$_2$O
Formula weight	1306.46
Crystal habit, color	rod, colorless
Crystal size (mm)	$0.5 \times 0.5 \times 1.0$
Crystal system	Monoclinic
Space group	$P2_1$
Unit cell dimensions	
a (Å)	15.155(1)
b (Å)	10.285(1)
c (Å)	20.906(1)
β (°)	109.86(1)
Volume (Å^3)	3064.8(1)
Z	2
D_{calcd} (g cm^{-3})	1.403
μ (mm^{-1})	0.14
$F(000)$	1370
Diffractometer	SMART CCD (Bruker)
Wavelength, MoKα (Å)	0.71073
Temperature (°C)	20
θ Range for data collection (°)	1.43–30.52
Resolution (Å)	0.70
Measured reflections	22,753
Unique reflections	11,746
Index ranges (°)	$0 \le h \le 21$, $-14 \le k \le 14$, $0 \le l \le 29$
Unique reflections [$F^2 > 2\sigma(F^2)$]	9127
Structure solution	Molecular replacement (PATSEE)
Refinement method	Full-matrix least-squares on F^2
Weighting scheme	$w = [S^2(F_o{}^2) + (1.1005P)^2 + 0.0487P]^{-1}$, where $P = (F_o{}^2 + 2F_c{}^2)/3$
Data/parameters	11746/888
R [$F^2 > 2\sigma(F^2)$]	R [a] = 0.055, wR [b] = 0.118
R (all data)	R [a] = 0.078, wR [b] = 0.133
Goodness-of-fit	1.065
Highest peak/deepest hole (e Å^{-3})	0.25/−0.20

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

[b] $wR = \Sigma\{w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2\}^{1/2}$.

Structure solution and refinement.—The crystal structure was solved by molecular replacement with PATSEE[7] using the crystal structure of β-CD–ethyleneglycol[8] as a phasing model. Only the atomic coordinates of the β-CD backbone (atoms C-1–C-5, O-2–O-5) were used for the calculations. The missing atoms, O-6, DMSO, and water molecules were located from difference Fourier electron density maps assisted by the graphic program XTALVIEW.[9] H-atom positions of β-CD and DMSO were calculated and treated according to the 'riding model'.[10] Some water H-atoms could be located from difference electron density maps. Anisotropic refinement by full-matrix least-squares on F^2 using SHELXL-97[10] was carried out for all non-H atoms. Some difficulties occurred in the course of refinement because of the disorder found in the β-CD cavity and water sites around the O-6–H groups of glucose units 4 and 5 (see below). The refinement of 888 parameters converged at an R-factor of 0.055 for 9,127 data with $F^2 > 2\sigma(F^2)$.

The fractional atomic coordinates and equivalent isotropic thermal displacement factors are listed in Table 2. The geometrical parameters are given in Table 3. The thermal ellipsoid plots in Fig. 1(a) and (b) were drawn by ORTEP-III.[11] Atomic labeling is used as in Ref. 12, i.e., C-43 denotes carbon atom 4 (C-4) of glucose unit 3, and the disordered atoms are additionally labeled with letters A and B (Fig. 4).

3. Results and discussion

Structural description of β-CD.—All glucose residues are in normal $^4C_1$ chair conformation as shown with the Cremer–Pople puckering parameter Q, θ[13] in the ranges 0.54–0.58 Å, 1–7°, respectively (Table 3). The β-CD adopts a 'round' conformation stabilized by intramolecular, interglucose O-3(n)···O-2($n+1$) hydrogen bonds with O···O separation 2.74–2.95 Å (Figs. 1–4, Table 3). This conformation is also shown by the torsion angles ϕ, ψ describing the orientation of glucose around the glycosidic bond in the ranges 102.6–119.1°, 118.6–139.1°, and an O-4($n+1$)–O-4(n)–O-4($n-1$) angle of 125.3–132.6° showing the well defined heptagon. However, the β-CD macrocycle exhibits some degree of distortion as shown with larger tilt angle of glucose units 1 (25.4°), 5 (19.2°), and high deviation of O-4 atoms from their common least squares plane up to 0.27 Å for glucose unit 4 (Table 3).

Torsion angles C-4–C-5–C-6–O-6, O-5–C-5–C-6–O-6 define the orientation of C-6–O-6 bond. All C-6–O-6 bonds are directed 'away' from the β-CD cavity as indicated by the corresponding angles in the ranges 50.0–59.6° and −61.4 to −67.6°, respectively (Table 3). Exceptions are disordered O-61A, O-65A, O-65B, O-67B which point 'inward' the cavity as shown with

Table 2
Fractional atomic coordinates and equivalent isotropic thermal displacement factors of β-CD·0.5DMSO·7.35H_2O

Atom	x/a	y/b	z/c	U_{eq} (Å^2)
C-11	0.5490(3)	0.5050(4)	−0.0423(2)	0.0595(9)
C-21	0.5460(2)	0.4746(4)	0.02702(19)	0.0592(9)
C-31	0.4630(2)	0.3879(4)	0.02182(16)	0.0511(7)
C-41	0.3726(2)	0.4451(3)	−0.02728(19)	0.0527(8)
C-51	0.3839(3)	0.4764(4)	−0.0956(2)	0.0642(10)
C-61	0.3016(4)	0.5459(6)	−0.1438(3)	0.1030(18)
O-21	0.63190(17)	0.4180(3)	0.06856(13)	0.0768(8)
O-31	0.45275(18)	0.3726(3)	0.08658(13)	0.0750(8)
O-41	0.30028(14)	0.3505(2)	−0.03648(12)	0.0534(5)
O-51	0.46349(17)	0.5605(3)	−0.08387(14)	0.0659(6)
O-61A [a]	0.3101(4)	0.5665(7)	−0.2069(3)	0.130(2)
O-61B [a]	0.2760(11)	0.6640(11)	−0.1246(9)	0.133(5)
C-12	0.2228(2)	0.3855(3)	−0.01640(17)	0.0506(8)
C-22	0.2016(2)	0.2718(3)	0.02219(16)	0.0503(8)
C-32	0.1705(2)	0.1548(3)	−0.02408(17)	0.0462(7)
C-42	0.0901(2)	0.1933(3)	−0.08741(16)	0.0418(6)
C-52	0.1107(2)	0.3136(3)	−0.12142(17)	0.0458(7)
C-62	0.0248(2)	0.3682(3)	−0.17572(18)	0.0549(8)
O-22	0.28118(17)	0.2396(3)	0.08030(13)	0.0657(7)
O-32	0.14310(17)	0.0506(2)	0.00993(12)	0.0599(6)
O-42	0.07550(14)	0.08585(19)	−0.13347(11)	0.0433(5)
O-52	0.14424(15)	0.4174(2)	−0.07286(12)	0.0517(5)
O-62	−0.04493(17)	0.4020(3)	−0.14752(14)	0.0672(7)
C-13	−0.0161(2)	0.0350(3)	−0.16223(16)	0.0460(7)
C-23	−0.0102(3)	−0.1117(3)	−0.15363(16)	0.0524(8)
C-33	0.0454(3)	−0.1693(3)	−0.19501(16)	0.0506(8)
C-43	0.0033(2)	−0.1258(3)	−0.26872(15)	0.0448(7)
C-53	−0.0031(2)	0.0218(3)	−0.27314(16)	0.0477(7)
C-63	−0.0503(3)	0.0737(4)	−0.34397(19)	0.0644(10)
O-23	0.0308(2)	−0.1406(3)	−0.08278(12)	0.0719(8)
O-33	0.0426(3)	−0.3071(2)	−0.19079(14)	0.0812(9)
O-43	0.06232(14)	−0.1738(2)	−0.30402(10)	0.0455(5)
O-53	−0.05569(15)	0.0679(2)	−0.23200(11)	0.0511(5)
O-63	−0.1424(2)	0.0276(4)	−0.37401(14)	0.0873(9)
C-14	0.0204(2)	−0.2484(4)	−0.36354(16)	0.0503(7)
C-24	0.0736(3)	−0.3762(3)	−0.35596(19)	0.0561(8)
C-34	0.1718(2)	−0.3531(3)	−0.35580(16)	0.0486(7)
C-44	0.1676(2)	−0.2770(3)	−0.41897(15)	0.0421(7)
C-54	0.1149(2)	−0.1502(3)	−0.42146(17)	0.0511(8)
C-64	0.1051(3)	−0.0692(4)	−0.4838(2)	0.0715(11)
O-24	0.0716(2)	−0.4424(3)	−0.29717(15)	0.0767(8)
O-34	0.2201(2)	−0.4728(3)	−0.35214(15)	0.0738(7)
O-44	0.26196(14)	−0.2511(2)	−0.41514(10)	0.0468(5)
O-54	0.02176(16)	−0.1800(3)	−0.42171(11)	0.0599(6)
O-64	0.0712(2)	−0.1371(3)	−0.54468(13)	0.0820(9)
C-15	0.2892(2)	−0.2810(3)	−0.47196(15)	0.0467(7)
C-25	0.3683(2)	−0.3782(3)	−0.44983(16)	0.0489(7)
C-35	0.4516(2)	−0.3195(3)	−0.39506(16)	0.0485(7)
C-45	0.4787(2)	−0.1916(3)	−0.41911(15)	0.0466(7)
C-55	0.3940(2)	−0.1010(3)	−0.44804(15)	0.0492(7)
C-65	0.4156(3)	0.0139(4)	−0.4843(2)	0.0751(11)
O-25	0.33887(18)	−0.4939(2)	−0.42541(13)	0.0605(6)
O-35	0.52874(18)	−0.4072(3)	−0.37686(14)	0.0682(7)

Table 2 (*Continued*)

Atom	x/a	y/b	z/c	U_{eq} (Å^2)
O-45	0.54551(14)	−0.1305(3)	−0.36102(10)	0.0526(6)
O-55	0.31829(15)	−0.1680(2)	−0.49673(10)	0.0510(5)
O-65A [b]	0.3334(5)	0.0931(6)	−0.5143(4)	0.094(2)
O-65B [b]	0.3630(16)	0.1293(16)	−0.4868(14)	0.099(6)
C-16	0.6386(2)	−0.1147(4)	−0.36007(16)	0.0519(8)
C-26	0.7039(2)	−0.1546(4)	−0.29044(17)	0.0563(8)
C-36	0.6914(2)	−0.0630(4)	−0.23682(15)	0.0520(8)
C-46	0.7044(2)	0.0751(4)	−0.25490(15)	0.0486(7)
C-56	0.6420(2)	0.1096(4)	−0.32719(16)	0.0513(8)
C-66	0.6630(3)	0.2391(4)	−0.35098(19)	0.0622(9)
O-26	0.68827(18)	−0.2871(3)	−0.27692(14)	0.0682(7)
O-36	0.75827(17)	−0.0938(3)	−0.17132(11)	0.0628(6)
O-46	0.68147(16)	0.1552(2)	−0.20611(11)	0.0550(6)
O-56	0.65579(16)	0.0153(3)	−0.37399(10)	0.0549(6)
O-66	0.75941(19)	0.2425(3)	−0.34487(15)	0.0742(7)
C-17	0.7385(3)	0.2643(4)	−0.17980(19)	0.0616(10)
C-27	0.7787(2)	0.2534(5)	−0.10320(19)	0.0631(10)
C-37	0.7028(2)	0.2701(4)	−0.07116(17)	0.0573(9)
C-47	0.6454(2)	0.3907(4)	−0.09809(18)	0.0589(9)
C-57	0.6061(3)	0.3866(4)	−0.17571(18)	0.0616(9)
C-67	0.5460(5)	0.4977(5)	−0.2099(3)	0.0936(16)
O-27	0.82400(18)	0.1302(3)	−0.08628(13)	0.0716(7)
O-37	0.7441(2)	0.2727(4)	0.00152(13)	0.0877(10)
O-47	0.56905(15)	0.3905(2)	−0.07106(12)	0.0548(6)
O-57	0.6849(2)	0.3792(3)	−0.19951(13)	0.0700(7)
O-67A [c]	0.5719(5)	0.6274(6)	−0.1997(3)	0.1083(18)
O-67B [c]	0.5009(6)	0.4701(9)	−0.2755(3)	0.086(3)
S-1 [d]	0.3715(6)	0.1444(9)	−0.2148(5)	0.244(4)
O-1 [d]	0.4513(12)	0.0576(16)	−0.2278(15)	0.286(13)
C-1 [d]	0.2747(8)	0.047(2)	−0.2168(12)	0.230(14)
C-2 [d]	0.3500(13)	0.2900(14)	−0.2625(11)	0.228(13)
W-1 [e]	0.3087(10)	0.0453(14)	−0.2764(8)	0.105(5)
W-2 [e]	0.3712(9)	−0.0763(9)	−0.2500(4)	0.079(4)
W-3 [e]	0.4144(5)	−0.2176(6)	−0.2054(3)	0.143(2)
W-4 [e]	0.4116(9)	0.2545(10)	−0.3843(7)	0.232(6)
W-5 [e]	0.2152(4)	0.3477(5)	−0.5238(2)	0.1190(13)
W-6 [e]	0.1798(4)	−0.0131(7)	−0.6184(3)	0.0530(18)
W-7 [e]	0.2261(14)	0.1507(17)	−0.6055(11)	0.140(7)
W-8 [e]	0.1309(17)	−0.0502(16)	−0.6389(11)	0.105(7)
W-9 [e]	−0.1172(4)	−0.1981(7)	−0.5729(3)	0.1346(17)
W-10 [e]	0.1473(11)	−0.6934(11)	−0.2820(7)	0.140(5)
W-11 [e]	−0.1451(3)	−0.4183(4)	−0.2493(2)	0.0752(9)
W-12 [e]	−0.167(2)	−0.393(2)	−0.177(2)	0.169(11)
W-13 [e]	0.0218(2)	0.6114(2)	−0.03709(14)	0.0679(7)

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[a] Occupancy factors of O-61A and O-61B are 0.7 and 0.3, respectively.

[b] Occupancy factors of O-65A and O-65B are 0.75 and 0.25, respectively.

[c] Occupancy factors of O-67A and O-67B are 0.65 and 0.35, respectively.

[d] Occupancy factor of DMSO is 0.5.

[e] Occupancy factors of water sites W-1 (0.25), W-2 (0.25), W-3 (0.75), W-4 (0.7), W-5 (1.0), W-6 (0.5), W-7 (0.25), W-8 (0.25) W-9 (1.0), W-10 (0.4), W-11 (0.8), W-12 (0.2), W-13 (1.0).

the angles −176.2°, 64.0°; 176.4°, 55.6°; −152.9°, 86.0°; −167.2°, 71.7°, respectively.

Inclusion geometry of DMSO in the β-CD cavity.— The DMSO molecule partially occupies the β-CD cavity (occupancy 0.5) and its S-atom is displaced from the center of O-4 plane to the β-CD O-6-side ca. 0.9 Å (Figs. 2 and 4). Theoretically, the DMSO geometry is a trigonal pyramid in which the O-atom can be located at

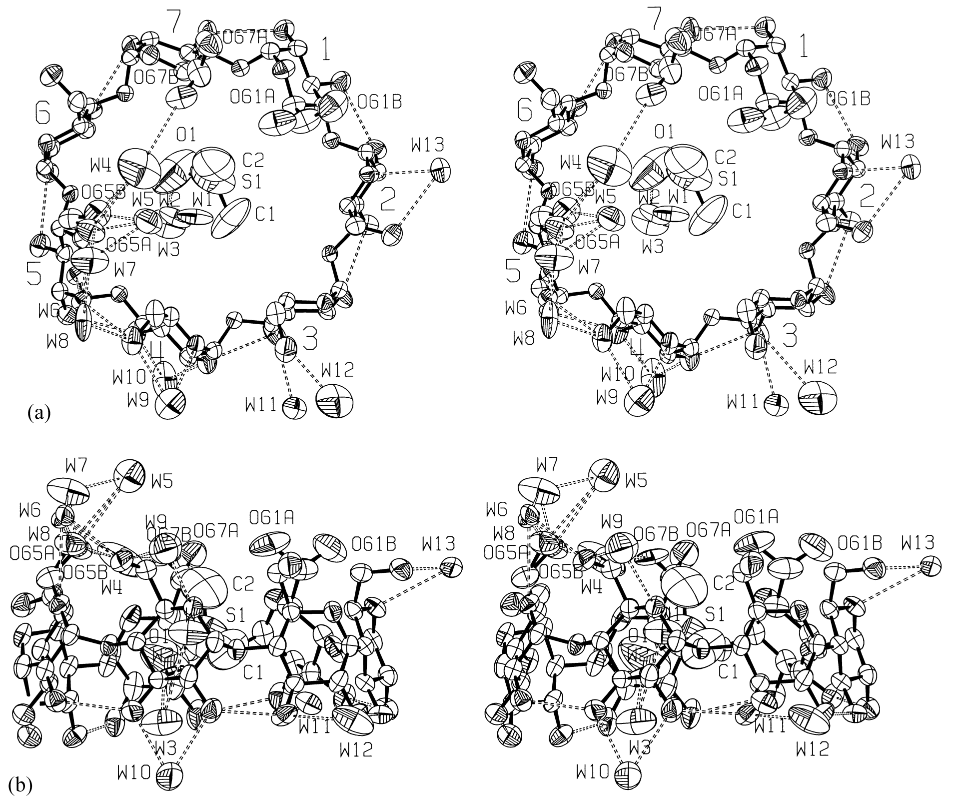

Fig. 1. ORTEP-III[11] stereo plot of the β-CD·0.5DMSO·7.35H$_2$O inclusion complex drawn with displacement ellipsoids at the 30% probability level: (a) top view, and (b) side view. Dashed lines indicate possible hydrogen bonds within O···O separation of 3.5 Å. O-61–H, O-65–H, and O-67–H groups are twofold disordered. All water sites are partially occupied (occupancies 0.2–0.8), except W-5, W-9, and W-13 (see also Table 2). Occupancy factor of DMSO is 0.5.

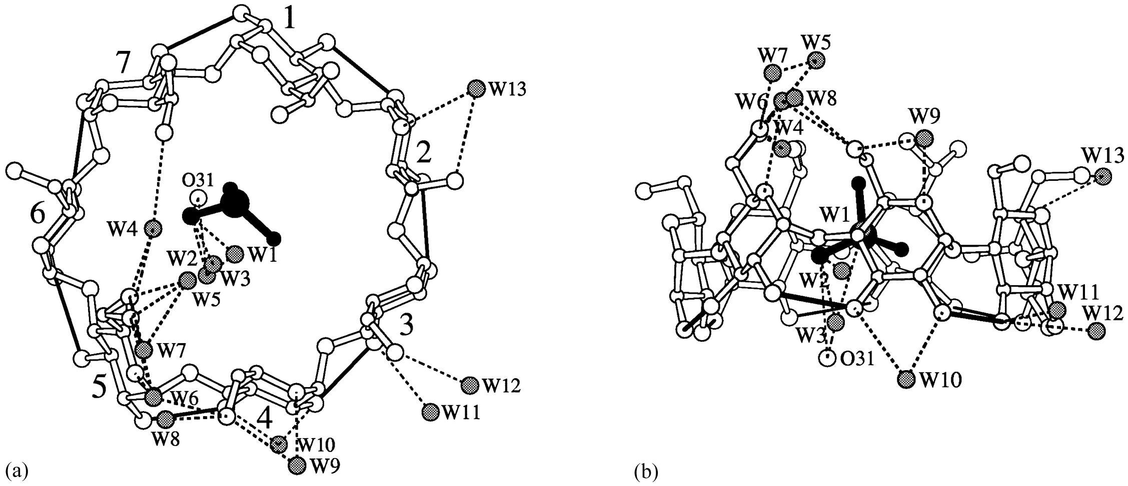

Fig. 2. Inclusion geometry of DMSO in the β-CD cavity: (a) top view, and (b) side view. Annular geometry of β-CD is stabilized by intramolecular, interglucose O-3(n)···O-2($n+1$) hydrogen bonds (solid lines). For clarity, β-CD is shown in white ball-and-stick and DMSO in black (small, bigger, and biggest balls are C, O, and S atoms, respectively), water sites in gray balls, and hydrogen atoms not shown. O–H···O hydrogen bonds are represented with dashed lines. O-31 ($-x+1$, $y-0.5$, $-z$) bridges DMSO O-atom and water site W-3 is shown with an isolated white ball. Drawn with MOLSCRIPT.[22]

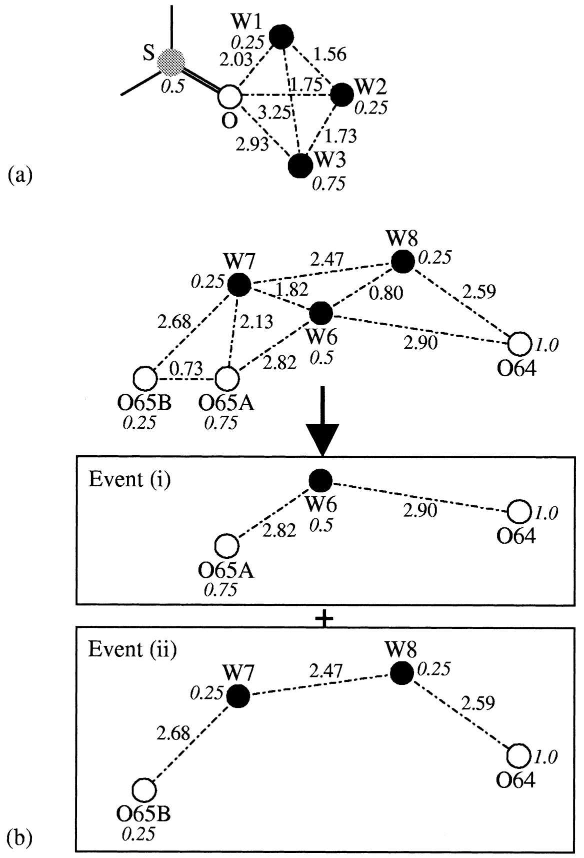

Fig. 3. Disorder phenomena occurred (a) in the β-CD cavity, and (b) around the O-64–H and O-65–H groups. In (a), water site W-2 cannot be occupied simultaneously with water sites W-1, W-3 and DMSO. In (b), water site W-6 is located synchronously with O-65A not with water sites W-7, W-8. Water O-atoms in black circles, β-CD O-6–H groups in white, and DMSO O^-, S-atoms in white, gray. Italic number beside the atomic name is an occupancy factor and the given distances are in Å. See text for more details.

any position around the pseudo threefold axis of the DMSO molecule. Since the bond distances of S=O (1.60 Å), and S–C (1.76 Å) are different, the O and C positions can be distinguished. It is found that one S–C bond points away from the O-4 plane and makes an angle of 13.6° with respect to the molecular axis of β-CD, and the S=O bond is directed below the O-4 plane (Figs. 1 and 2). DMSO is maintained in position by hydrogen bonding to the water site W-3 and O-31–H group of a symmetry equivalent β-CD with O···O distances 2.95 and 3.40 Å, respectively (Figs. 2–4). The inclusion geometry of DMSO in the present structure is different from that observed in the corresponding complex of α-CD[4] as in the latter, only one S–C bond of DMSO is included in the α-CD cavity at the O-2-, O-3-side and is slanted 65.6° to the α-CD molecular axis.

Disorder phenomena.—Disorder found inside the β-CD cavity should be noted. Fig. 3(a) shows that water site W-2 cannot be occupied simultaneously with water sites W-1, W-3, and DMSO because the involved interatomic distances are too short, 1.56–2.03 Å. In addition, water site W-3 is only coexistent with water site W-1 or with DMSO molecule. This is because W-3···O_{DMSO}, W-3···W-1 distances are 2.93, 3.25 Å—long enough to be accounted for hydrogen bond interactions while W-1···O_{DMSO} distance is too short, 2.03 Å. Disordered water molecules linked to O-64–H and O-65–H (depicted in Fig. 3(b)). The water cluster W-6–W-7–W-8 has a sum of occupancy 1.0 and the distances W-6–W-7 (1.82 Å), W-6–W-8 (0.80 Å) are too short. This can be interpreted as the events (i) O-65A···W-6···O-64 and (ii) O-65B···W-7···W-8···O-64 which are not coexistent. In addition, the distance between water sites W-11 and W-12 of 1.68 Å and their occupancies sum up to 1.0 suggesting that they cannot be occupied concurrently (Figs. 1 and 2, Table 2).

Disordered water molecules.—7.35 water molecules were found distributed over 13 positions, both inside (W-1–W-4) and outside (W-5–W-13) the β-CD cavity. All water sites were partially occupied (occupancies 0.2–0.8), except for water sites W-5, W-9, and W-13 which were fully occupied. In the β-CD cavity, water site W-1 is not coexistent with DMSO because the W-1···O_{DMSO} distance is too short, 2.03 Å (Fig. 3(a)). Therefore, water site W-3 links W-1 or DMSO O-atom via hydrogen bonding (Fig. 3(a)). Water site W-4 bridges the disordered O-65A and O-67B (Figs. 1 and 4). In the crystal lattice, the water sites play a significant role as hydrogen bonding mediators in stabilizing the crystal structure (Fig. 4). They maintain the orientation of O-6–H groups by bridging to O-5, e.g., O-51···W-3···O-61A, O-52···W-13···O-62, O-54···W-9···O-64, and link symmetry related β-CD molecules, e.g., O-21$(-x+1, y-0.5, -z)$···W-3(x, y, z)···O-61A$(x, y-1, z)$, O-22$(-x, y-0.5, z)$···W-12(x, y, z)···O-62$(x, y-1, z)$ (see Fig. 4). In addition, the O-2–H and O-6–H groups of β-CD are systematically hydrated by neighboring water sites, viz., W-3, W-12, W-13, W-8, W-4, W-7, W-13 for O-2–H; W-3, W-11, W-5, W-9, W-7, W-6, W-4 for O-6–H (Fig. 4). The corresponding O···O distances are in ranges 2.69–3.46 and 2.59–3.50 Å, respectively.

Crystal packing.—In the present crystal structure, β-CD molecules are stacked in 'herring-bone' style[14] and both ends of β-CD cavity are blocked by adjacent, symmetry-related β-CD molecules, as generally found in the crystal structures of β-CD with small guest molecules.[15] It should be noted that the guest DMSO has no effect on the packing of the host β-CD. The crystal space groups of β-CD hydrates[16–18] and of DMSO inclusion complex are $P2_1$ with comparable unit cell constants and unit cell volume, since the DMSO is completely included in the β-CD cavity. This contrasts to the corresponding complexes of α-CD[4,19–21]

Table 3
Geometrical parameters of β-CD·0.5C_2H_6SO·7.35H_2O (distances in Å and angles in deg)

Residue	1	2	3	4	5	6	7
Q [a], θ [b]	0.56, 3	0.54, 4	0.57, 1	0.58, 4	0.55, 5	0.56, 3	0.57, 7
ϕ [c], ψ [c]	109.4(3), 133.0(3)	102.6(3), 118.6(3)	107.8(3), 128.3(3)	111.5(3), 126.3(3)	119.1(3), 129.7(3)	103.8(3), 113.7(3)	116.1(3), 139.1(3)
Tilt angle [d]	25.4(2)	9.9(2)	7.1(1)	10.5(2)	19.2(2)	4.4(2)	15.5(2)
O-4 angle [e]	127.8(1)	125.3(1)	132.6(1)	127.8(1)	125.3(1)	130.7(1)	128.8(1)
Distances							
O-4 deviation [f]	0.09	−0.20	−0.04	0.27	−0.13	−0.18	0.19
O-3(*n*)···O-2(*n*+1)	2.90(1)	2.88(1)	2.78(1)	2.74(1)	2.88(1)	2.87(1)	2.95(1)
Torsion angle							
C-4–C-5–C-6–O-6	−176.2(5) [g] 59.4(10) [g]	59.6(4)	58.7(4)	50.0(5)	176.7(4) [g] −152.9(12) [g]	56.0(4)	54.1(6) [g] −167.2(5) [g]
O-5–C-5–C-6–O-6	64.0(6) [g] −60.3(9) [g]	−61.4(3)	−62.6(4)	−70.3(4)	55.6(5) [g] 86.0(12) [g]	−64.5(3)	−67.(6) [g] 71.7(6) [g]

[a] Cremer–Pople puckering amplitude.[13]

[b] Indicates the deviation from the theoretical chair conformation (ideal value: $\theta = 0$).

[c] Torsion angles ϕ and ψ at glycosidic O-4, defined as O-5(*n*)–C-1(*n*)–O-4(*n*−1)–C-4(*n*−1) and C-1(*n*)–O-4(*n*−1)–C-4(*n*−1)–C-3(*n*−1), respectively.

[d] Tilt angles, defined as the angles between the O-4 plane and the planes through C-1(*n*), C-4(*n*), O-4(*n*) and O-4(*n*−1).

[e] Angle at each glycosidic O-4: O-4(*n*+1)–O-4(*n*)–O-4(*n*−1).

[f] Deviation of O-4 atoms from the least-squares plane through the seven O-4 atoms.

[g] Values for twofold disordered O-6 with the occupancy factors 0.7, 0.3; 0.75, 0.25; 0.65, 0.35 for sites A, B of glucose residues 1, 5, 7, respectively.

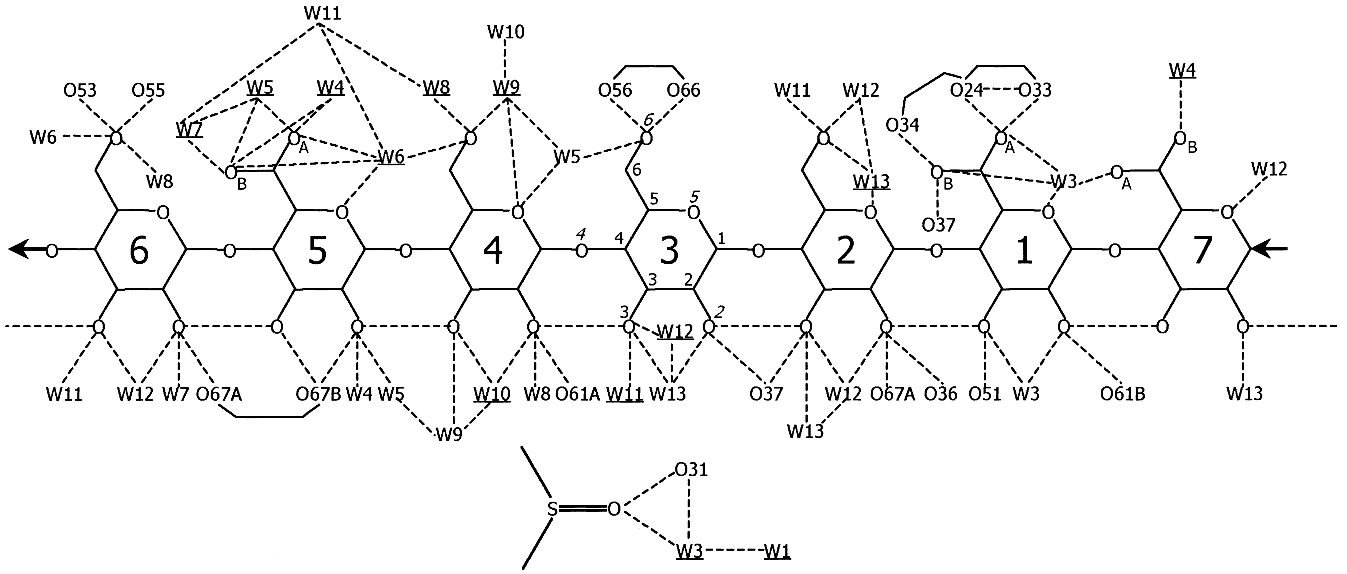

Fig. 4. Schematic O–H···O hydrogen bonds in the crystal structure of the β-CD·0.5DMSO·7.35H_2O inclusion complex. Dashed lines represent possible hydrogen bonds within O···O separation of 3.5 Å. Arrows indicate the connection between glucose units of β-CD. Underlined atomic names showing atoms in the general position: *x*, *y*, *z*; other atoms are in the symmetry related positions. Atomic numbering is shown in glucose unit 3. Normal numbers 1–6 indicate carbon atoms and italic numbers *2–6* oxygen atoms.

because in the DMSO complex,[4] DMSO is only partially included in the α-CD cavity. The crystal space groups and packing mode of α-CD hydrates[19–21] are $P2_12_12_1$ and ‘herring-bone’,[14] while those of DMSO complex[4] are $P2_1$ and ‘brick’.[14]

4. Supplementary material

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CSD-185494. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html or from the CCDC, 12 Union Road, Cambridge, CB2, IEZ, UK (tel. + 44 1223 336408; fax: + 44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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