Carbohydrate Research, 107 (1982) 7–16
Elsevier Scientific Publishing Company, Amsterdam – Printed in The Netherlands

CRYSTAL AND MOLECULAR STRUCTURES OF CYCLOMALTOHEPTAOSE INCLUSION COMPLEXES WITH HI AND WITH METHANOL*

KLAUS LINDNER AND WOLFRAM SAENGER

Max-Planck-Institut für experimentelle Medizin, Abteilung Chemie, Hermann-Rein-Str. 3, D-3400 Göttingen (West Germany)

(Received July 6th, 1981; accepted for publication, December 16th, 1981)

ABSTRACT

β-Cyclodextrin (β-CD; cyclomaltoheptaose; cyclohepta-amylose; $C_{42}H_{70}O_{35}$) crystallises from aqueous solutions of HI and of MeOH in the form of stout prisms, which are isomorphous to each other with monoclinic space-group $P2_1$; cell constants for $C_{42}H_{70}O_{35} \cdot 2HI \cdot 8\ H_2O$: $a = 21.25(3)$, $b = 10.28(2)$, $c = 15.30(2)$ Å, $\beta = 113.25(9)°$, and $Z = 2$; and for $C_{42}H_{70}O_{35} \cdot MeOH \cdot 6.5\ H_2O$: $a = 21.03(3)$, $b = 10.11(2)$, $c = 15.33(2)$ Å, $\beta = 111.02(9)°$, and $Z = 2$. X-Ray counter data were used to determine the structures of both crystals, which belong to the cage type, with β-CD molecules in nearly identical, "round" shapes. In the HI complex, one I^- is located inside, and one outside, the β-CD cavity; in the MeOH complex, the MeOH is within the cavity. The cavity is closed at the O-2,O-3 side by adjacent β-CD molecules, and at the O-6 side by water molecules hydrogen-bonded to the guest and to surrounding β-CD molecules. Interstices between β-CD molecules are filled by water of hydration molecules in distorted co-ordination.

INTRODUCTION

The doughnut-shaped cyclodextrin molecules, a family consisting of six (α), seven (β), or eight (γ) α-D-glucopyranosyl residues, have been the subject of several studies during the past ten years, with the smallest, α-cyclodextrin (α-CD), being most intensively investigated[1–3]. We now report on two β-CD inclusion complexes that are highly isomorphous to the recently described "empty" β-CD · dodecahydrate crystallised from pure water[4] and with the β-CD · EtOH · 8 H_2O obtained from aqueous ethanol[5].

EXPERIMENTAL

The HI complex of β-CD was crystallised according to a published procedure[6]. HI was freshly purified by distillation from hypophosphoric acid, and the samples

*Topography of Cyclodextrin Inclusion Complexes, Part XVIII. For Part XVII, see ref. 9.

0008-6215/82/0000–0000/$ 02.75,

TABLE I

β-CYCLODEXTRIN METHANOL–WATER COMPLEX: FRACTIONAL ATOMIC CO-ORDINATES AND ISOTROPIC TEMPERATURE FACTORS[a] (STANDARD DEVIATIONS IN PARENTHESES APPLY TO THE LAST DIGIT GIVEN)

Atom[b]	x	y	z	*B*	*Atom*	x	y	z	*B*
C-1(1)	.5492(4)	.5334(9)	.1006(6)	3.5(3)	O-4(1)	.5432(3)	.3835(6)	−.1558(3)	3.1(2)
C-2(1)	.4788(4)	.5100(10)	.0261(6)	3.8(3)	O-5(1)	.5927(3)	.5845(6)	.0579(4)	3.6(2)
C-3(1)	.4836(4)	.4191(10)	−.0527(5)	3.2(3)	O-6(1)	.6418(5)	.6861(11)	−.0801(6)	8.4(4)
C-4(1)	.5351(4)	.4770(9)	−.0900(6)	3.1(3)	O-2(2)	.5850(3)	.1543(7)	.4146(4)	4.3(2)
C-5(1)	.6028(4)	.4982(10)	−.0113(6)	3.3(3)	O-3(2)	.5005(3)	.2901(8)	.2442(4)	4.9(2)
C-6(1)	.6595(6)	.5607(12)	−.0411(7)	5.3(4)	O-4(2)	.5740(3)	.4123(6)	.1453(4)	3.1(2)
C-1(2)	.6817(4)	.2871(11)	.4205(6)	3.8(3)	O-5(2)	.7025(3)	.4006(7)	.3846(4)	3.8(2)
C-2(2)	.6040(4)	.2763(11)	.3849(6)	3.7(3)	O-6(2)A	.7770(14)	.4932(43)	.2740(25)	10.9(15)
C-3(2)	.5742(4)	.2875(10)	.2777(6)	3.4(3)	O-6(2)B	.6988(5)	.6430(9)	.2724(7)	5.6(3)
C-4(2)	.6016(4)	.4116(10)	.2471(5)	3.3(3)	O-2(3)	.7731(3)	−.2789(7)	.4611(5)	4.3(2)
C-5(2)	.6788(4)	.4015(10)	.2825(6)	3.7(3)	O-3(3)	.6690(3)	−.0760(7)	.4358(4)	4.1(2)
C-6(2)	.7167(5)	.5149(12)	.2552(6)	5.1(3)	O-4(3)	.7068(3)	.1713(7)	.3913(4)	3.3(2)
C-1(3)	.8584(4)	−.1070(10)	.4999(6)	3.3(3)	O-5(3)	.8727(3)	.0259(7)	.5298(4)	3.6(2)
C-2(3)	.7872(4)	−.1462(11)	.4949(6)	3.7(3)	O-6(3)	.8452(4)	.2594(9)	.6059(5)	5.5(3)
C-3(3)	.7352(4)	−.0499(10)	.4314(6)	3.3(3)	O-2(4)	.9229(3)	−.4918(7)	.2641(4)	4.1(2)
C-4(3)	.7544(4)	.0902(10)	.4623(5)	3.1(2)	O-3(4)	.8789(3)	−.4037(7)	.4109(4)	4.2(2)
C-5(3)	.8266(4)	.1208(9)	.4701(5)	3.1(3)	O-4(4)	.8602(3)	−.1215(7)	.4080(3)	3.2(2)
C-6(3)	.8526(5)	.2539(11)	.5153(7)	4.5(3)	O-5(4)	.9957(3)	−.1585(7)	.3126(4)	3.5(2)
C-1(4)	.9707(4)	−.2734(10)	.2593(5)	3.2(3)	O-6(4)	1.0062(5)	.1140(9)	.3441(6)	7.7(4)
C-2(4)	.9490(4)	−.3735(10)	.3178(6)	3.3(3)	O-2(5)	.8004(3)	−.4310(7)	−.1261(4)	4.9(2)

C-3(4)	.8958(4)	−.3125(10)	.3490(6)	3.1(3)	O-3(5)	.8530(3)	−.4654(7)	.0728(4)	4.4(2)
C-4(4)	.9187(4)	−.1827(9)	.3994(5)	3.1(2)	O-4(5)	.9131(3)	−.2424(7)	.1794(3)	3.2(2)
C-5(4)	.9465(4)	−.0896(10)	.3414(6)	3.2(3)	O-5(5)	.9202(3)	−.1559(7)	−.0503(4)	4.0(2)
C-6(4)	.9839(5)	.0276(12)	.3975(8)	5.1(4)	O-6(5)	1.0414(3)	−.1133(9)	.1188(5)	6.0(3)
C-1(5)	.8642(4)	−.2289(11)	−.1100(6)	3.5(3)	O-2(6)	.5795(3)	−.1235(7)	−.3678(4)	4.2(2)
C-2(5)	.8586(4)	−.3604(10)	−.0658(5)	3.5(3)	O-3(6)	.6843(4)	−.2897(7)	−.2389(5)	5.0(2)
C-3(5)	.8555(4)	−.3425(9)	.0309(5)	3.1(3)	O-4(6)	.8024(3)	−.1573(6)	−.1271(3)	3.2(2)
C-4(5)	.9177(4)	−.2638(10)	.0898(5)	3.0(2)	O-5(6)	.7324(3)	.0774(7)	−.3226(4)	3.4(2)
C-5(5)	.9175(4)	−.1296(10)	.0428(6)	3.8(3)	O-6(6)	.8737(3)	.0290(9)	−.2729(5)	5.6(3)
C-6(5)	.9783(5)	−.0436(12)	.0958(7)	4.8(3)	O-2(7)	.4231(3)	.2876(7)	−.2907(4)	4.0(2)
C-1(6)	.6625(4)	.0471(9)	−.3478(6)	3.3(3)	O-3(7)	.4906(3)	.0862(7)	−.3611(4)	3.7(2)
C-2(6)	.6510(4)	−.1004(10)	−.3428(6)	3.5(3)	O-4(7)	.6349(3)	.1094(6)	−.2845(3)	2.7(2)
C-3(6)	.6921(4)	−.1506(9)	−.2433(6)	3.4(3)	O-5(7)	.5819(3)	.4524(6)	−.2729(4)	3.0(2)
C-4(6)	.7656(4)	−.1134(10)	−.2210(5)	3.0(2)	O-6(7)	.6502(3)	.4375(8)	−.3954(4)	4.4(2)
C-5(6)	.7738(4)	.0366(9)	−.2289(6)	3.2(3)	O-W-1	.5399(3)	−.3640(7)	−.4466(4)	4.5(2)
C-6(6)	.8445(5)	.0843(11)	−.2113(7)	4.4(3)	O-W-2	.9791(4)	−.1469(10)	.7640(6)	7.5(3)
C-1(7)	.5242(4)	.4238(9)	−.2505(6)	3.1(3)	O-W-3	.7590(5)	.5890(14)	.6012(7)	11.6(5)
C-2(7)	.4832(4)	.3118(9)	−.3117(5)	3.1(3)	O-W-4	.8838(5)	.5027(13)	.7094(7)	9.1(4)
C-3(7)	.5266(4)	.1890(9)	−.2984(5)	3.0(2)	O-Me	.2996(5)	.3132(12)	−.1172(9)	10.9(5)
C-4(7)	.5910(4)	.2224(9)	−.3160(5)	2.7(2)	C-Me	.2528(7)	.4096(21)	−.1496(13)	10.6(7)
C-5(7)	.6277(4)	.3412(9)	−.2618(6)	3.1(3)	O-W-7	1.0725(5)	−.1822(11)	−.0379(7)	8.6(4)
C-6(7)	.6817(5)	.3931(10)	−.2981(6)	3.8(3)	O-W-5	.8621(12)	.2421(19)	.2629(22)	18.0(16)
O-2(1)	.4347(3)	.4519(8)	.0703(4)	4.4(2)	O-W-6	.7763(10)	−.6971(21)	−.0539(18)	12.2(10)
O-3(1)	.4199(3)	.4126(8)	−.1277(4)	4.6(2)					

[a] $B(A^2)$ calculated from deposited anisotropic factors of the form $T = \exp -(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)$. [b] C-1 in glucosyl residue I *etc.*; O-W, water; O-Me, methanol.

TABLE II

β-CYCLODEXTRIN · 2HI · 8H_2O COMPLEX: FRACTIONAL ATOMIC CO-ORDINATES AND ISOTROPIC TEMPERATURE FACTORS[a] (STANDARD DEVIATIONS IN PARENTHESES APPLY TO THE LAST DIGIT GIVEN)

Atom[b]	x	y	z	*B*	*Atom*	x	y	z	*B*
C-1(1)	.5501(5)	.5490(13)	.0817(7)	2.7(4)	O-4(1)	.5436(4)	.3872(7)	−.1687(5)	2.1(2)
C-2(1)	.4797(5)	.5259(11)	.0034(7)	2.4(4)	O-5(1)	.5952(4)	.5959(8)	.0445(5)	2.6(3)
C-3(1)	.4855(5)	.4349(12)	−.0688(7)	2.3(4)	O-6(1)	.6359(5)	.6858(11)	−.1055(7)	5.2(4)
C-4(1)	.5361(5)	.4854(11)	−.1037(7)	2.1(4)	O-2(2)	.5898(4)	.1730(9)	.4012(5)	3.1(3)
C-5(1)	.6047(6)	.5078(12)	−.0226(8)	2.5(4)	O-3(2)	.5029(4)	.3221(10)	.2357(6)	4.4(3)
C-6(1)	.6595(5)	.5706(17)	−.0529(8)	3.3(4)	O-4(2)	.5727(4)	.4277(8)	.1296(5)	2.2(2)
C-1(2)	.6869(6)	.2970(13)	.4095(8)	2.6(4)	O-5(2)	.7089(4)	.4051(8)	.3729(5)	2.2(2)
C-2(2)	.6089(5)	.2940(12)	.3716(8)	2.3(4)	O-6(2)	.7040(4)	.6405(8)	.2643(6)	3.0(3)
C-3(2)	.5742(6)	.3111(12)	.2642(8)	2.4(4)	O-2(3)	.7579(4)	−.2679(8)	.4484(5)	2.7(3)
C-4(2)	.6041(5)	.4259(11)	.2313(7)	2.1(3)	O-3(3)	.6629(4)	−.0570(8)	.4209(5)	2.6(3)
C-5(2)	.6809(5)	.4070(12)	.2690(8)	2.5(4)	O-4(3)	.7098(3)	.1788(8)	.3812(4)	1.8(2)
C-6(2)	.7187(6)	.5120(13)	.2404(8)	2.8(4)	O-5(3)	.8699(3)	.0147(7)	.5304(5)	1.9(2)
C-1(3)	.8503(6)	−.1128(11)	.4973(7)	2.2(4)	O-6(3)	.8585(4)	.2449(9)	.6079(5)	3.4(3)
C-2(3)	.7769(5)	−.1387(12)	.4861(7)	2.1(3)	O-2(4)	.9174(4)	−.4848(8)	.2600(5)	2.5(3)
C-3(3)	.7292(5)	−.0401(12)	.4212(7)	1.7(3)	O-3(4)	.8733(4)	−.4094(8)	.4093(5)	2.8(3)
C-4(3)	.7540(5)	.0965(11)	.4537(7)	1.9(3)	O-4(4)	.8514(3)	−.1327(8)	.4057(5)	2.1(2)
C-5(3)	.8285(5)	.1138(11)	.4661(7)	1.9(3)	O-5(4)	.9879(3)	−.1633(8)	.3223(5)	2.2(2)
C-6(3)	.8577(6)	.2406(13)	.5149(10)	3.0(5)	O-6(4)	.9875(5)	.1156(9)	.3517(7)	4.3(4)
C-1(4)	.9637(5)	−.2757(11)	.2651(7)	2.0(3)	O-2(5)	.8058(4)	−.4102(8)	−.1395(5)	2.6(2)

C-2(4)	.9419(5)	−.3747(11)	.3203(7)	1.8(3)	O-3(5)	.8565(4)	−.4594(9)	.0601(5)	3.6(3)
C-3(4)	.8874(5)	−.3185(12)	.3484(7)	2.2(3)	O-4(5)	.9068(3)	−.2469(8)	.1818(5)	1.9(2)
C-4(4)	.9108(5)	−.1898(12)	.4012(7)	2.1(3)	O-5(5)	.9188(4)	−.1335(8)	−.0409(5)	2.5(3)
C-5(4)	.9371(5)	−.0995(12)	.3464(8)	2.1(4)	O-6(5)	1.0352(4)	−.0995(9)	.1257(6)	3.4(3)
C-6(4)	.9755(6)	.0169(13)	.4069(8)	3.1(4)	O-2(6)	.5787(3)	−.1064(8)	−.3877(5)	2.5(2)
C-1(5)	.8642(5)	−.2058(12)	−.1106(7)	2.0(3)	O-3(6)	.6835(4)	−.2754(8)	−.2574(7)	3.7(3)
C-2(5)	.8628(5)	−.3404(11)	−.0724(7)	2.1(4)	O-4(6)	.8025(3)	−.1444(8)	−.1314(5)	2.0(2)
C-3(5)	.8557(5)	−.3329(12)	.0241(7)	2.1(3)	O-5(6)	.7307(3)	.0864(8)	−.3315(4)	1.9(2)
C-4(5)	.9157(5)	−.2541(11)	.0927(7)	1.8(3)	O-6(6)	.8767(4)	.0264(8)	−.2660(5)	3.0(3)
C-5(5)	.9135(5)	−.1201(11)	.0521(7)	1.9(3)	O-2(7)	.4269(4)	.2773(8)	−.3046(5)	2.5(3)
C-6(5)	.9724(6)	−.0359(13)	.1110(8)	3.1(4)	O-3(7)	.4908(3)	.0905(8)	−.3792(5)	2.6(2)
C-1(6)	.6620(5)	.0584(13)	−.3589(6)	1.9(3)	O-4(7)	.6353(3)	.1165(7)	−.2972(5)	1.8(2)
C-2(6)	.6498(5)	−.0891(11)	−.3574(7)	2.0(3)	O-5(7)	.5813(4)	.4488(7)	−.2872(5)	2.3(2)
C-3(6)	.6902(5)	−.1365(11)	−.2604(8)	2.0(4)	O-6(7)	.6645(6)	.4160(11)	−.3877(7)	5.9(4)
C-4(6)	.7666(6)	−.1024(11)	−.2275(8)	2.1(4)	O-W-1	1.0044(5)	−.6086(12)	.1872(7)	5.7(4)
C-5(6)	.7735(5)	.0437(11)	−.2353(7)	1.8(3)	O-W-2	1.0553(4)	−.2008(10)	−.0215(7)	4.6(4)
C-6(6)	.8460(5)	.0871(11)	−.2117(8)	2.8(4)	O-W-3	.3027(4)	.3421(9)	−.1668(6)	3.7(3)
C-1(7)	.5231(5)	.4201(12)	−.2670(8)	2.3(4)	O-W-4	.5310(4)	−.3568(8)	−.4258(5)	2.9(3)
C-2(7)	.4832(5)	.3093(11)	−.3289(7)	2.0(3)	O-W-5	1.1830(5)	−.1844(10)	.0536(8)	5.6(4)
C-3(7)	.5292(5)	.1902(11)	−.3132(7)	2.0(3)	O-W-6	.2770(6)	.3483(10)	−.0228(8)	6.4(5)
C-4(7)	.5918(5)	.2248(10)	−.3280(7)	1.4(3)	O-W-7	.6598(6)	.6353(12)	−.4968(9)	7.6(5)
C-5(7)	.6291(5)	.3410(11)	−.2676(7)	2.0(3)	O-W-8	.8708(7)	−.7210(11)	.2810(10)	8.4(6)
C-6(7)	.6874(6)	.3888(12)	−.2885(10)	2.8(4)	I-1	.8532(0)	−.4365(3)	−.3295(1)	3.7(0)
O-2(1)	.4354(4)	.4750(10)	.0436(6)	3.8(3)	I-2	.2818(1)	.6793(3)	−.0483(1)	9.5(1)
O-3(1)	.4199(4)	.4204(9)	−.1515(5)	3.3(3)					

[a]B(A^2) as given as footnote in Table I. [b]C-1 in glucosyl residue 1, *etc.*; O-W, water; I-1 and I-2, iodide.

were prepared in a cold room in order to avoid decomposition of β-CD. The MeOH complex was obtained by allowing a 60% aqueous MeOH solution saturated at boiling temperature with β-CD to cool slowly.

Because crystals of β-CD tend to dry out under ambient conditions, they were mounted in quartz capillaries together with some mother liquor. X-Ray diffraction data were collected with an automated STOE four-circle diffractometer employing graphite-monochromatised MoKα radiation for the HI adduct and Ni-filtered CuKα radiation for the MeOH complex. Data were corrected empirically for absorption effects[7] and converted into normalised structure amplitudes E_h. The structure of the β-CD · HI · 8 H_2O complex was determined by both Patterson and direct methods[8], and refined by full-matrix, least-squares cycles to a final R-factor of 6.5% for all the 5036 measured data weighted according to counting statistics and employing anisotropic thermal parameters. The known positions of C and O atoms were then used to solve the structure of the isomorphous MeOH adduct which, after location of water and MeOH atoms by difference Fourier techniques, refined to an R-factor of 7% for all 4643 measured data. Hydrogen atoms for water and β-CD hydroxyl groups could not be positioned with certainty and were therefore omitted from the refinement, whereas C-H hydrogen atoms were put at calculated positions and used in refinements with isotropic thermal parameters. Final atomic co-ordinates and isotropic temperature factors (calculated from anisotropic ones) are given in Tables I and II; lists of structure amplitudes and comprehensive atomic parameters have been deposited with the data file*.

In the β-CD · 2 HI · 8 H_2O complex, all atoms are fully ordered, whereas, in β-CD · MeOH · 6.5 H_2O, HO-6 of D-glucose 2 and two water molecules, O-W-5 and O-W-6, are only partially occupied as follows: O-6(2A), 0.31(2); O-6(2B), 0.79(3); O-W-5, 0.66(3); and O-W-6, 0.50(2); all other occupancies are 1.0.

DISCUSSION

Both adducts described here belong to the cage type, with β-CD rings arranged in herring-bone fashion due to the twofold screw axis. This organisation leads to closure of β-CD cavities by adjacent β-CD molecules on both sides, in contrast with the "open" channel structures.

All glucosyl residues are in the $^4C_1$ conformation, and the ring of intramolecular hydrogen-bonds between HO-2 and HO-3 of adjacent glucosyl residues is always fully established, with mean O-2_n ··· O-3_{n+1} distances of 2.86(7) Å for β-CD · MeOH · 6.5 H_2O and 2.90(15) Å for β-CD · 2 HI · 8 H_2O. In the latter case, the standard deviation is higher than in the former and reflects more variation in O-2 ··· O-3 distances, probably brought about by protonation of water molecules by HI. The

*Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33872 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, Great Britain.

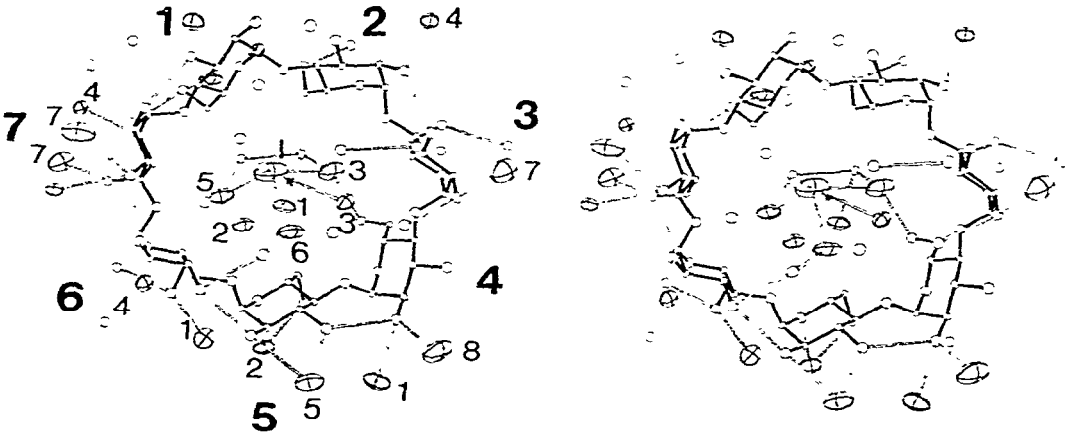

Fig. 1. Stereodiagram of β-CD · HI · $8H_2O$, showing water molecules and I^- as ellipsoids, and β-CD C and O atoms as spheres. Hydrogen-bonding contacts are indicated by open lines[12]. Figures in bold face refer to glucosyl residues, other figures are for water molecules as listed in Table II, and I stands for iodide ion.

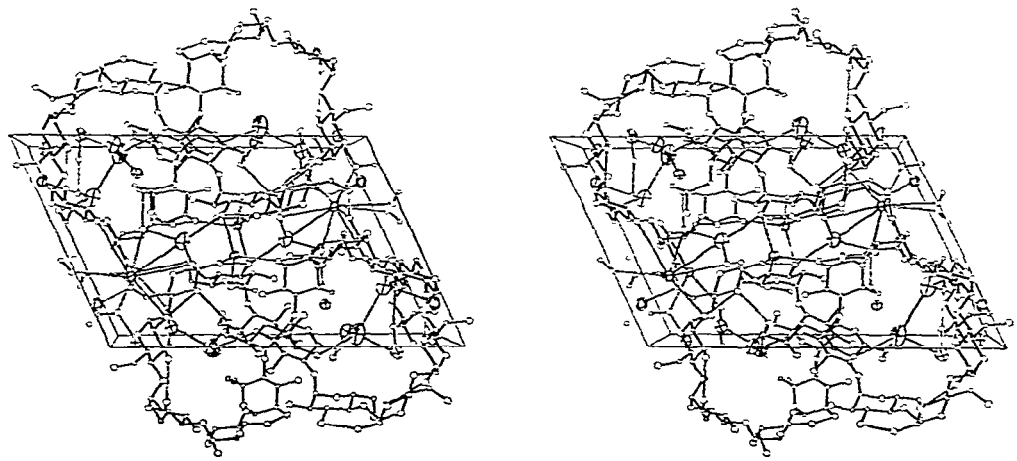

Fig. 2. Packing diagram of β-CD · HI · $8H_2O$, looking down the *b*-axis. Graphical details as in Fig. 1.

only major difference between the two β-CD molecules described here lies in the orientation of the C-6–O-6 bonds. In general, these are turned "away" from the center of the molecule, corresponding to the (—)*gauche* conformation of the O-5–C-5–C-6–O-6 group. In the MeOH complex, one of these bonds is in the (+)*gauche* range, whereas, in the HI complex, two of these bonds are turned towards the center of the molecule in order to form hydrogen bonds with enclosed water molecules (Figs. 1 and 3).

Bond angles and distances are not given explicitly, because they are in overall agreement with those described in greater detail for the crystal structure of β-CD ·

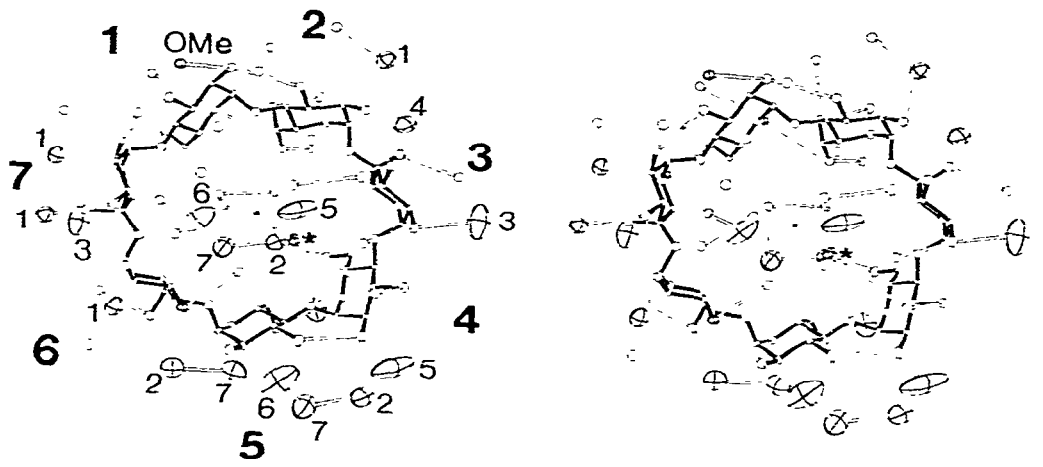

Fig. 3. Stereodiagram of β-CD · MeOH · 6.5H_2O, looking onto the plane defined by O-4 atoms and nearly along the axis of the MeOH molecule (*). Note that MeOH is pushed towards the "right-hand" side of the cavity; the MeOH hydroxyl faces the viewer and is hydrogen-bonded to hydroxyls of adjacent β-CD molecules whereas the methyl group is located within the cavity and opposes two water molecules that display excessive thermal vibration and/or disorder. Graphical details as in Fig. 1; the MeOH hydroxyl located outside the cavity is indicated by OMe.

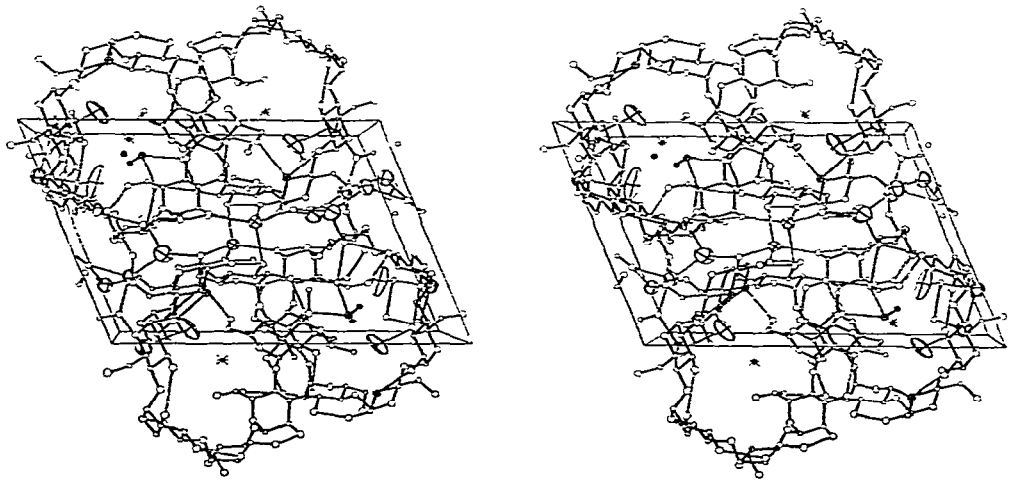

Fig. 4. Packing diagram of β-CD · MeOH · 6.5H_2O, looking down the *b*-axis. Graphical details as in Fig. 1.

dodecahydrate[9]. Besides these, geometrical details concerning the shape of the macrocycle are comparable and suggest that the circular structure of β-CD is rather "rigid", due to the well-established ring of hydrogen bonds between HO-2 and HO-3 of adjacent glucosyl residues.

The packing schemes of the HI · 8 H_2O and MeOH · 6.5 H_2O complexes of β-CD are comparable not only for the β-CD hosts but also for some water of hydration

molecules located near the O-6 side of β-CD molecules and in the interstices between β-CD molecules. Major differences are seen around guest molecules, within the cavity, and around the I^- located between β-CD molecules. This is also evident from the co-ordination scheme for the two I^-, the one inside the β-CD cavity being 5-fold co-ordinated with $I^- \cdots O$ distances in the range 3.37–4.02 Å, whereas the one accommodated in interstices is 9-fold co-ordinated with oxygen atoms at distances 3.42–4.19 Å. Assuming hydrogen-bonding interactions of the type $I^- \cdots H\text{-}O$, the van der Waals contact distance computes[10] to 4.35 Å, suggesting that all of these short distances are probably hydrogen bonds.

In the β-CD · MeOH · 6.5 H_2O complex, the MeOH molecule is located within the β-CD cavity and oriented along the axis of the annulus, but shifted sideways such that it is in van der Waals contact with the atoms of the cavity. The MeOH hydroxyl is hydrogen-bonded to a disordered HO-6 of an adjacent β-CD molecule and to HO-3 of another β-CD molecule, all hydroxyls being located near the O-2,O-3 rim of the enclosing β-CD molecule. The methyl group of MeOH points into the β-CD cavity, facing two water molecules that display excessive thermal motion or even disorder, probably in order to fill empty space within the β-CD cavity (Figs. 3 and 4).

The inclusion geometry of β-CD · MeOH · 6.5 H_2O is largely different from that of the β-CD · EtOH · 8 H_2O complex. In the latter, the enclosed EtOH is distributed over two sites in nearly antiparallel orientation, with ethyl groups and one water molecule positioned in the cavity, whereas EtOH hydroxyls are hydrogen-bonded to β-CD hydroxyls and to water on both the O-2, O-3, and O-6 sides of the cavity. Common to both MeOH and EtOH complexes with β-CD, however, is the close contact of guest molecules with atoms lining the β-CD cavity.

Comparing the β-CD · MeOH · 6.5 H_2O complex with the α-CD · MeOH · 5 H_2O analogue[11], it is found that the situation is different again, with the smaller (5.2 Å *versus* 7 Å in β-CD) cavity filled by one MeOH molecule statistically disordered over two sites; one is hydrogen-bonded with two HO-6 groups of the host α-CD, whereas the other is located within the α-CD cavity and in no obvious hydrogen-bonding contact with hydroxyl groups or with water.

In addition, we should add that, in the "empty" β-CD · 12 H_2O complex, the enclosed 6.5 water molecules are statistically disordered over 9 sites and display rather large thermal motion. On inclusion of a guest molecule, it appears that the disorder is greatly reduced, and replaced by more well-defined locations of enclosed guest and water molecules.

Comparison of the HI and MeOH adducts with β-CD described here with the uncomplexed, "empty" β-CD · 12 H_2O reveals that, in contrast to the smaller α-CD molecule[1], β-CD is more rigid, maintaining its "round" shape under a variety of conditions. This finding suggests that, for β-CD, release of strain energy cannot be a major driving-force for adduct formation, but rather, hydrophobic forces and expulsion of "activated water" from the cavity have to be invoked[3].

REFERENCES

1 W. SAENGER, *Jerusalem Symp. Quantum Chem. Biochem.*, 8 (1976) 265–405.
2 W. SAENGER, *Angew. Chem. Int. Ed. Engl.*, 19 (1980) 344–362.
3 M. L. BENDER AND M. KOMIYAMA, *Cyclodextrin Chemistry*, Springer–Verlag, Berlin, 1978.
4 K. LINDNER AND W. SAENGER, *Angew. Chem. Int. Ed. Engl.*, 17 (1978) 694–695.
5 R. TOKUOKA, M. ABE, T. FUJIWARA, K.-I. TOMITA, AND W. SAENGER, *Chem. Lett.*, (1980) 491–494.
6 J. SZEJTLI AND Z. S. BUDAI, *Acta Chim. Acad. Sci. Hung.*, 94 (1977) 383–391.
7 A. C. T. NORTH, D. C. PHILLIPS, AND F. S. MATTHEWS, *Acta Crystallogr., Sect. A.*, 24 (1968) 351–359.
8 P. MAIN, L. LESSINGER, M. M. WOOLFSON, G. GERMAIN, AND J. P. DECLERCQ, *MULTAN, a System of Computer Programs for the Automatic Solution of Noncentrosymmetric Crystal Structures*, Universities of York (Great Britain) and Louvain (Belgium), 1977.
9 K. LINDNER AND W. SAENGER, *Carbohydr. Res.*, 99 (1982) 103–115.
10 R. C. WEAST, *CRC Handbook of Chemistry and Physics*, CRC Press, Cleveland, Ohio, 1977, p. D-178.
11 B. HINGERTY AND W. SAENGER, *J. Am. Chem. Soc.*, 98 (1976) 3357–3365.
12 C. K. JOHNSON, Report ORNL-3794, Oak Ridge National Laboratory, Tennessee, 1965.