Crystal Structures of the Inclusion Complexes of β-Cyclodextrin with Aliphatic Monoacids Tridecanoic Acid and (Z)-Tetradec-7-enoic Acid. Formation of [3]Pseudorotaxanes

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Abstract. The structures of the inclusion complexes of beta cyclodextrin with the aliphatic monoacids tridecanoic acid (**1**) and (Z)-tetradec-7-enoic acid (**2**) have been determined at room temperature. Both compounds crystallise in $P1$, $a = 15.654(6)$ Å, $b = 15.650(6)$ Å, $c = 15.937(6)$ Å, $\alpha = 101.58(1)°$, $\beta = 101.59(1)°$, $\gamma = 103.58(1)°$, $Z = 1$, for **1** and $a = 15.6259(9)$ Å, $b = 15.623(1)$ Å, $c = 15.935(1)$ Å, $\alpha = 101.547(2)°$, $\beta = 101.555(2)°$, $\gamma = 103.642(2)°$, $Z = 1$, for **2**. One molecule of the monoacids threads through two cyclodextrin macrocycles arranged in dimers thus forming [3]pseudorotaxanes. The host dimers are aligned along a channel in order to create a hydrophobic environment for the terminal methyl group of the guest and isolate it from the aqueous environment that surrounds the cyclodextrin dimeric units. The guests exhibit disorder over two orientations resulting in hydrogen bonding between the carboxyl groups of adjacent guest molecules along the channel and formation of carboxylic dimers. This crystal packing differs from that of β-CD complexes of homologous dicarboxylic acids.

1. Introduction

The purpose of crystal engineering has been defined as the understanding of intermolecular interactions in the context of crystal packing and the utilisation of that knowledge to the design of new materials with desirable characteristics [1]. This is done by introducing into the building blocks of suitable functional groups with the ability to interact by non-covalent intermolecular interactions resulting in recognition and self-association. Thus the primary concepts of supramolecular

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chemistry [2] are used to achieve a high level of organisation and predict the crystal structure.

In the present study, the common recognition motif of the carboxylic dimer has been selected to build the supramolecular arrangement of β-cyclodextrin (β-CD) channels [3]. β-CD is a cyclic oligosaccharide [4], consisting of seven α-1,4-D-glucopyranose units with a cavity that preferentially binds to lipophilic guest molecules of suitable size, forming inclusion complexes in aqueous solutions. This process by which the guest molecule is protected from the aqueous environment inside the hydrophobic cavity of the macrocyclic host is spontaneous and involves non-covalent host-guest interactions. β-CD has the tendency to form dimers [5] that have a longer cavity and this is particularly helpful in the case of elongated guests as the long aliphatic acids. In the systems reported here, one molecule of a long aliphatic monocarboxylic acid threads through two β-cyclodextrin macrocycles associated via H-bonds to form a [3]pseudorotaxane [6]. While rotaxanes are mechanically interlocked compounds with bulky stopper groups added to the thread's extremities to prevent its unthreading, pseudorotaxanes differ in that they lack the stopper groups. Unthreading is possible but it can be prevented in a suitable environment [7]. The crystal structures of the complexes of tridecanoic acid and (Z)-tetradec-7-enoic acid with β-CD are part of a systematic investigation of the way in which the nature, size and end groups of an aliphatic guest influence the crystal packing of β-CD inclusion complexes [3, 5, 8] as well as those of α-cyclodextrin [9], a host with a narrower cavity, more suitable for the binding of unbranched aliphatic compounds. By employing the regular and, up to a point, predictable self-assembly of the complexes of these natural molecular receptors, it is possible to build systems with a variety of supramolecular organisation.

2. Experimental

2.1. PREPARATION AND CRYSTALLISATION

The complexes were prepared by addition of tridecanoic acid or (Z)-tetradec-7-enoic acid to an aqueous solution of β-CD, at a host/guest molar ratio of 1:1. The precipitates were redissolved in a mixture of water/ethanol, 3/1 approximately, at 70 °C and were allowed to cool slowly over a period of 7 days at the end of which colourless diamond shaped crystals were formed. The crystals were twins but they could be divided into single crystals.

2.2. STRUCTURE ANALYSIS

Single crystals were separated and sealed into a glass capillary to avoid water loss that would destroy them. Data were collected on a Crystal Logic four-circle diffractometer, equipped with a fine focus sealed tube, with graphite monochromated

Mo$K\alpha$ radiation (λ = 0.71069 Å) with θ-2θ scans. No absorption correction was applied but the data were corrected for Lorentz and polarisation effects.

2.2.1. β-CD + Tridecanoic Acid

The cell dimensions were obtained by least-squares analysis of 16 reflections in the range of $11° < 2\theta < 22°$. A hemisphere of data was collected to $2\theta \approx 41°$ with a speed of 3.0 °/min. Three standard reflections, monitored every 97 reflections, showed a decay of 1.5% in intensity during data collection for which the data were corrected.

The asymmetric unit contains two monomers of β-CD, A and B and one molecule of tridecanoic acid (as in Figure 1). The structure was solved by isomorphous molecular replacement using the coordinates of the glucosidic skeleton of the isomorphous complex β-CD + 3,5-dimethylbenzoic acid [10]. The rest of the host atoms and the some of the co-crystallised water molecules were found by subsequent difference Fourier calculations and the structure was refined isotropically by full-matrix least-squares refinement based on F^2 (SHELX97) [11a] up to an R-factor of 13.5%. During the refinement cycles three oxygen atoms from the primary side of molecule A and two of molecule B were found to be disordered. Their occupancy, as that of any partially occupied atom in the refinements of both structures, was refined independently of their thermal parameters. Subsequently, C(6), O(6) (Figure 2) and the water molecules found so far, were assigned anisotropic thermal parameters and calculated hydrogen atoms were added to the carbon atoms of the host, having $U_{\text{eq}} = 1.2U_{\text{eq}'}$ of the corresponding atom. A difference electron density Fourier method gave two possible positions for the guest molecule. Because of the weak diffraction of the crystal at high 2θ and, consequently, of the limited amount of reflections, it was not possible to refine individually all the parameters of the guest atoms. Therefore, its geometry was optimised by fitting the two models of the guest into the difference electron density Fourier map using the graphics program "O" [12]. The occupancy factor of the guest was refined to 52% and 48% for the proposed models. The structure was then refined exhaustively by weighted full matrix least-squares refinement. The application of diffuse solvent correction improved the statistics. Before the end of the refinement the coordinates of the guests were subjected to rigid body refinement along with the thermal parameters of the individual atoms. The refinement converged to an R-factor of 8.62% (Table I).

2.2.2. β-CD + (Z)-Tetradec-7-enoic Acid

The cell dimensions were obtained by the least-squares fit of 28 reflections in the range of $11° < 2\theta < 24°$. A hemisphere of data was collected to $2\theta \approx 42°$ with a speed of 4.5 °/min. Three standard reflections, monitored every 97 reflections, showed no decay in intensity during data collection.

Table I. Crystal data and structure refinement

	β-CD/Tridecanoic acid	β-CD/(Z)-Tetradec-7-enoic acid
Molecular formula	$(C_{42}H_{70}O_{35})_2 \cdot C_{13}H_{26}O_2 \cdot (H_2O)_{19.5}$	$(C_{42}H_{70}O_{35})_2 \cdot C_{14}H_{26}O_2 \cdot (H_2O)_{14.9}$
Formula weight	2835.6	2764.8
Temperature	293(2) K	293(2) K
Wavelength	0.71069 Å	0.71069 Å
Space group	$P1$	$P1$
a, α	15.654(6)Å, 101.58(1)°	15.625(9)Å, 101.547(2)°
b, β	15.650(6)Å, 101.59(1)°	15.623(1)Å, 101.555(2)°
c, γ	15.937(6)Å, 103.58(1)°	15.935(1)Å, 103.642(2)°
Volume/Z	3589(2)Å^3/1	3576.4(4)Å^3/1
Density (calculated)	1.286 Mg/m^3	1.283 Mg/m^3
2θ range for data collection	4.2°–41°	2.7°–42°
Index ranges	$-15 \le h \le 0, -15 \le k \le 15, -15 \le l \le 15$	$-15 \le h \le 15, -15 \le k \le 0, -15 \le l \le 16$
Reflections collected/independent	7574/7565	8017/8012
Solution method	Isomorphous molecular replacement[10]	Isomorphous molecular replacement[13]
Refinement method	Full-matrix least-squares on F^2	Full-matrix-block least-squares on F^2
Data/restraints/parameters	7565/3/1069	8004/0/1108
Goodness of fit on $F^2(S)$	1.000	1.088
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0862, wR_2 = 0.2313$	$R_1 = 0.0862, wR_2 = 0.2505$
R indices (all data)	$R_1 = 0.1142, wR_2 = 0.2702$	$R_1 = 0.1018, wR_2 = 0.2567$
Largest diff. peak and hole	0.393 and -0.343 e Å^{-3}	0.493 and -0.418 e Å^{-3}
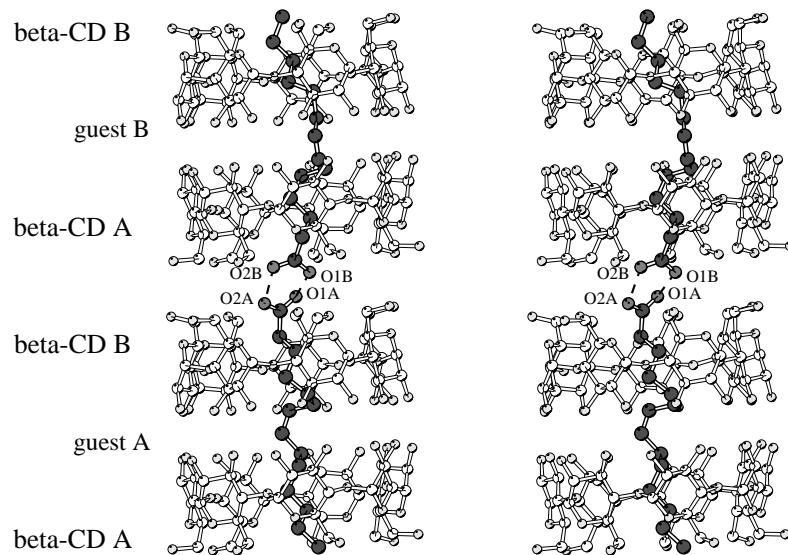
Figure 1. Stereo view [17] of the channel packing of the complex of β-CD/(*Z*)-tetradec-7-enoic acid. The guest molecules disordered over two orientations interact through hydrogen bonds forming a carboxylic dimer.

The structure was solved using the coordinates of the skeleton atoms of the isomorphous complex β-CD – 4-*tert*-butyltoluene [13]. The asymmetric unit is a β-CD dimer and one molecule of (*Z*)-tetradec-7-enoic acid disordered over two orientations. The package *SHELX93* [11b] was used for all computations and refinement was based on F^2. Difference electron density Fourier maps revealed the missing hydroxyl oxygen atoms and C(6) carbon atoms of β-CD as well as water oxygen atoms. Hydrogen atoms were calculated for all carbon atoms of β-CD using a riding model with U_{eq} (H) = $1.2U_{eq'}$ of the corresponding carbon atoms. Anisotropic displacement parameters were assigned to hydroxyl O(2), O(3), O(6) atoms and most of the water oxygen atoms which behaved well during the refinement. The difference electron density corresponding to the guest molecules was defined very well inside the β-CD cavity. However, due to the disorder, some atoms were very closely located in the two models and the resulting geometry of the models was distorted. Thus geometries were optimised by fitting into the difference electron density map with the graphics program "*O*" [12] and they were
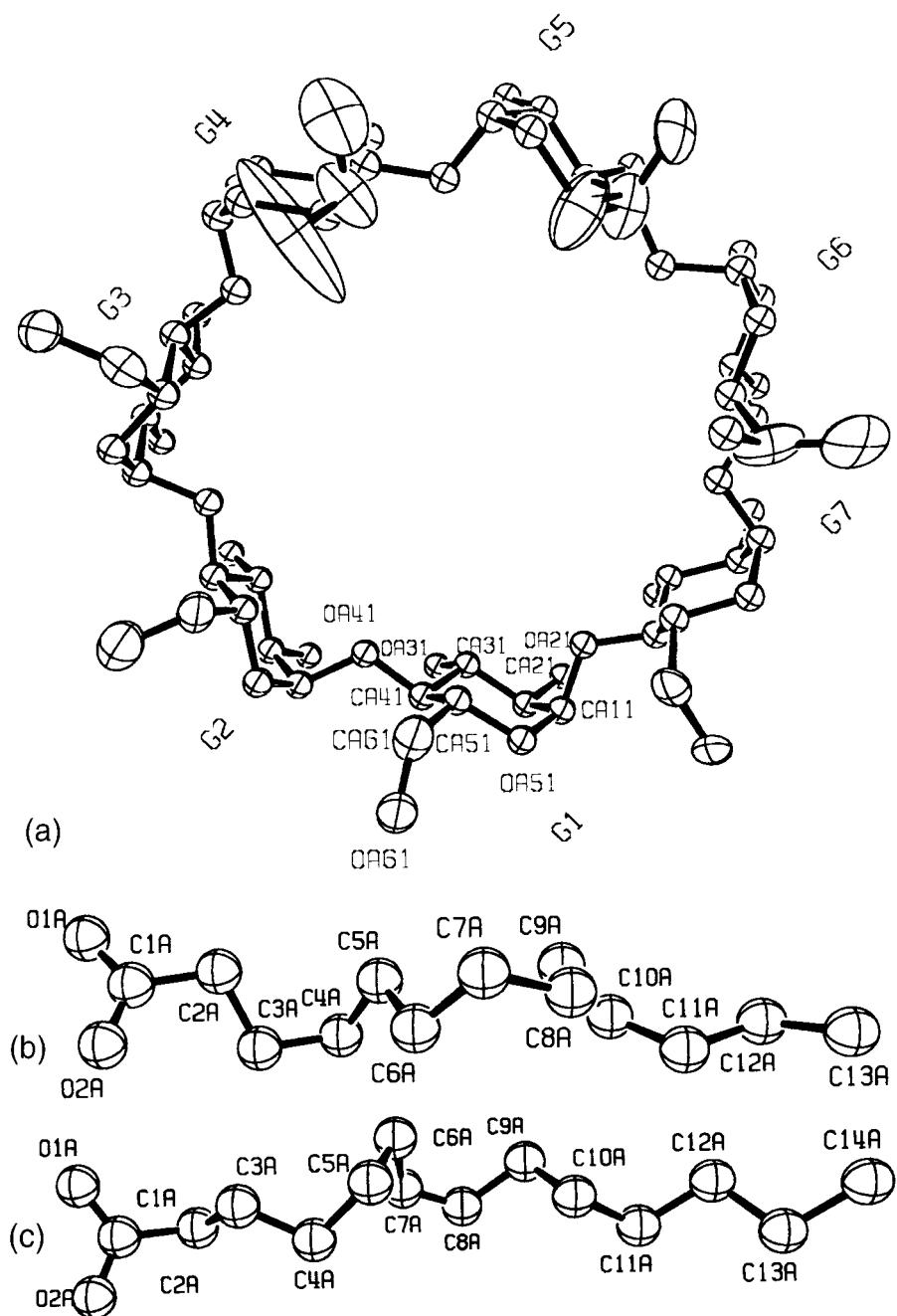
Figure 2. Ortep diagrams of (a) molecule A of β-cyclodextrin of the complex β-CD/tridecanoic acid showing the numbering scheme of the host, (b) *guest A* orientation of tridecanoic acid, (c) *guest A* orientation of (Z)-tetradec-7-enoic acid.

not refined further. The occupancy factors were refined to 51% and 49% for the two orientations. Towards the end of the refinement the guest atoms were assigned hydrogen atoms and their isotropic temperature factors were refined. The refinement converged to an R-factor of 8.62% (Table I).

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No CCDC182/991, 12 Union Road, Cambridge CB2 1EZ UK (fax: Int code +(1223) 336-033, e-mail: deposit@chemcrys.cam.ac.uk).

3. Results and Discussion

Crystallographic data are summarised in Table I. Final atomic coordinates and thermal parameters of the non-hydrogen atoms are given in Tables II and III. Both inclusion complexes comprise dimers of β-CD formed by H-bonds between the O(3) secondary hydroxyl groups [5] of the crystallographically independent β-CD monomers A and B (Figure 1). One molecule of the aliphatic monocarboxylic acid enters the β-CD dimer cavity and spans its entire length. The numbering scheme for the host and guest molecules is given in Figure 2; C(A or Bmn) and O(A or Bmn) denote the mth atom within the nth glucosidic residue (Gn) of the crystallographically independent β-CD molecules A and B. The inclusion complexes thus formed align along the **c** crystallographic axis to form channels (Figure 1). The crystallographic asymmetric unit contains one dimeric complex with the guest disordered over two orientations (*guest A* and *guest B*) with occupancy factors very close to 50% for both complexes (Tables II and III). Therefore, along the channel a β-CD dimer encloses one molecule of the aliphatic acid in orientation A (*guest A*) and the adjacent β-CD dimer in orientation B (*guest B*) in such a way that the guest molecules form conventional carboxylic dimers.

3.1. DESCRIPTION OF THE MACROCYCLE

The geometry of the host molecules of both complexes is undistorted retaining the shape of a regular heptagon (Figure 2a). The mean value of the angle between the glucosidic oxygen atoms O(4n − 1))$\cdots$O4(n)$\cdots$O(4(n + 1)) is 128° for both complexes, close to the angle of a regular heptagon (128.57°) (Table IV). The deviations of the glucosidic oxygen atoms from their mean plane are close to zero (Table IV). The regular shape of the macrocycles is retained due to intramolecular hydrogen bonds between the secondary hydroxyl groups O(3n)$\cdots$O(2(n + 1)) of each monomer (Table IV). The glucose rings retain the $^4C_1$ conformation and tilt regularly with respect to the 7-fold axis (Table IV). All primary hydroxyl groups of the β-CD/(Z)-tetradec-7-enoic acid complex point towards the exterior of the cavity (gauche-gauche orientation), while in residues G4, G5 and G6 of molecule A and G4 and G6 of molecule B of the β-CD/tridecanoic acid complex they are dis-

Table II. Positional ($\times 10^4$) and equivalent isotropic displacement parameters ($\mathring{A}^2 \times 10^3$) for the β-CD/tridecanoic acid complex (**1**). U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor. Occupancy factors (K) are given when different from one.

Atom	x	y	z	U_{eq}	K
C(A11)	4300(10)	8274(10)	7311(9)	68(4)	
C(A21)	4625(10)	8719(10)	6640(10)	68(4)	
O(A21)	4019(8)	8322(8)	5782(7)	85(3)	
C(A31)	5570(9)	8633(10)	6618(9)	61(3)	
O(A31)	5909(7)	9124(7)	6023(7)	77(3)	
C(A41)	6193(10)	9048(11)	7537(10)	72(4)	
C(A51)	5831(11)	8573(11)	8182(10)	76(4)	
O(A41)	7078(7)	8920(7)	7501(6)	73(3)	
O(A51)	4903(8)	8628(7)	8164(7)	83(3)	
C(A61)	6379(14)	8940(18)	9132(11)	116(7)	
O(A61)	6399(11)	9807(15)	9482(11)	178(9)	
C(A12)	7878(11)	9681(11)	7890(10)	74(4)	
C(A22)	8373(11)	9755(11)	7196(10)	76(4)	
O(A22)	7835(8)	9880(8)	6422(7)	88(3)	
C(A32)	8738(10)	8924(10)	6988(9)	66(4)	
O(A32)	9260(7)	9023(7)	6349(7)	76(3)	
C(A42)	9270(10)	8871(10)	7827(9)	64(4)	
C(A52)	8753(11)	8802(11)	8498(11)	76(4)	
O(A42)	9534(6)	8014(6)	7609(6)	69(2)	
O(A52)	8391(7)	9580(7)	8639(7)	77(3)	
C(A62)	9227(13)	8761(15)	9357(11)	95(5)	
O(A62)	9997(11)	9475(13)	9761(9)	130(5)	
C(A13)	10487(10)	8045(10)	7865(9)	65(4)	
C(A23)	10655(10)	7535(9)	7047(9)	63(4)	
O(A23)	10531(7)	7964(7)	6350(7)	76(3)	
C(A33)	10098(9)	6553(8)	6788(8)	56(3)	
O(A33)	10329(7)	6039(7)	6069(6)	73(3)	
C(A43)	10290(10)	6152(9)	7583(9)	58(3)	
C(A53)	10166(10)	6735(9)	8401(9)	65(4)	
O(A43)	9645(7)	5260(7)	7329(7)	76(3)	
O(A53)	10665(6)	7668(6)	8573(6)	65(2)	
C(A63)	10496(13)	6457(11)	9244(9)	82(5)	
O(A63)	11444(9)	6523(8)	9419(7)	92(3)	
C(A14)	9983(11)	4512(10)	7472(10)	73(4)	
C(A24)	9683(10)	3781(10)	6629(10)	72(4)	
O(A24)	10009(7)	4131(7)	5958(7)	81(3)	
C(A34)	8645(10)	3390(10)	6337(9)	65(4)	

Table II. (continued)

Atom	x	y	z	U_{eq}	K
O(A34)	8398(7)	2649(7)	5552(7)	78(3)	
C(A44)	8319(11)	3072(11)	7089(10)	76(4)	
C(A54)	8638(12)	3834(12)	7908(11)	88(5)	
O(A44)	7341(7)	2725(7)	6815(6)	73(3)	
O(A54)	9616(8)	4180(8)	8152(8)	95(3)	
C(A64)	8390(2)	3521(18)	8685(15)	147(11)	
O(A64)	8660(3)	2870(3)	8881(17)	191(15)	0.66
O(A64)	(88309)	4140(6)	9500(4)	480(12)	0.34
C(A15)	6937(10)	1821(10)	6853(9)	66(4)	
C(A25)	6269(10)	1331(10)	5972(9)	65(4)	
O(A25)	6693(7)	1294(7)	5270(7)	78(3)	
C(A35)	5517(10)	1787(10)	5820(9)	64(4)	
O(A35)	4839(7)	1268(7)	5029(7)	75(3)	
C(A45)	5090(10)	1794(10)	6597(9)	68(4)	
C(A55)	5799(11)	2279(12)	7479(11)	81(4)	
O(A45)	4455(7)	2347(6)	6464(6)	73(3)	
O(A55)	6519(7)	1853(7)	7554(7)	80(3)	
C(A65)	5424(17)	2150(2)	8249(12)	130(9)	
O(A65)	6010(4)	2500(7)	9050(5)	180(3)	0.28
O(A65)	5130(13)	1242(17)	8292(13)	126(7)	0.72
C(A16)	3514(10)	1937(11)	6489(10)	74(4)	
C(A26)	2906(11)	2024(10)	5681(10)	71(4)	
O(A26)	3053(8)	1529(7)	4890(7)	86(3)	
C(A36)	2980(10)	2989(10)	5686(9)	66(4)	
O(A36)	2339(8)	3031(7)	4923(7)	85(3)	
C(A46)	2819(11)	3476(10)	6525(9)	69(4)	
C(A56)	3456(12)	3368(11)	7344(10)	79(4)	
O(A46)	3006(6)	4417(6)	6553(6)	67(2)	
O(A56)	3372(7)	2424(7)	7270(7)	85(3)	
C(A66)	3160(3)	3670(2)	8155(14)	154(12)	
O(A66)	2280(3)	3160(2)	8170(2)	250(2)	0.69
O(A66)	3900(7)	3780(7)	8900(7)	230(4)	0.31
C(A17)	2283(10)	4838(10)	6640(9)	64(4)	
C(A27)	2172(10)	5324(10)	5916(9)	69(4)	
O(A27)	1892(7)	4676(7)	5053(7)	79(3)	
C(A37)	3038(11)	6050(10)	6000(10)	72(4)	
O(A37)	2922(7)	6515(7)	5326(7)	79(3)	
C(A47)	3277(10)	6700(10)	6903(9)	68(4)	
C(A57)	3370(10)	6214(10)	7641(9)	68(4)	
O(A47)	4188(6)	7329(6)	7026(6)	64(2)	

Table II. (continued)

Atom	x	y	z	U_{eq}	K
O(A57)	2521(7)	5485(7)	7467(6)	73(3)	
C(A67)	3471(14)	6821(13)	8541(10)	94(5)	
O(A67)	2796(9)	7283(8)	8569(8)	99(4)	
C(B11)	3165(11)	7138(11)	2248(10)	77(4)	
C(B21)	2732(11)	6817(10)	2907(10)	75(4)	
O(B21)	3131(8)	7457(7)	3759(7)	83(3)	
C(B31)	2804(10)	5873(9)	2926(9)	60(3)	
O(B31)	2303(7)	5544(7)	3533(7)	78(3)	
C(B41)	2409(11)	5259(10)	2018(10)	72(4)	
C(B51)	2861(11)	5633(10)	1375(10)	71(4)	
O(B41)	2531(7)	4376(7)	2046(6)	72(3)	
O(B51)	2823(7)	6529(7)	1391(7)	79(3)	
C(B61)	2480(2)	5103(12)	398(12)	134(11)	
O(B61)	1616(15)	5044(12)	67(13)	183(10)	
C(B12)	1765(11)	3584(10)	1680(10)	72(4)	
C(B22)	1687(11)	3078(10)	2369(10)	71(4)	
O(B22)	1577(8)	3623(8)	3150(7)	86(3)	
C(B32)	2511(10)	2713(9)	2572(9)	59(3)	
O(B32)	2408(7)	2167(7)	3184(7)	77(3)	
C(B42)	2584(10)	2176(10)	1733(9)	65(4)	
C(B52)	2656(11)	2706(11)	1067(10)	73(4)	
O(B42)	3437(6)	1909(6)	1942(6)	70(3)	
O(B52)	1865(7)	3050(7)	910(7)	78(3)	
C(B62)	2688(16)	2211(14)	153(11)	102(6)	
O(B62)	1942(12)	1432(9)	−217(8)	119(5)	
C(B13)	3396(10)	977(9)	1686(9)	59(3)	
C(B23)	3905(9)	777(9)	2505(8)	56(3)	
O(B23)	3506(7)	929(7)	3215(6)	73(3)	
C(B33)	4901(9)	1352(10)	2756(9)	62(3)	
O(B33)	5403(7)	1120(7)	3488(7)	73(3)	
C(B43)	5269(10)	1152(10)	1972(10)	69(4)	
C(B53)	4718(10)	1305(11)	1149(10)	72(4)	
O(B43)	6205(7)	1818(7)	2233(6)	72(3)	
O(B53)	3777(6)	774(6)	983(6)	67(2)	
C(B63)	5014(12)	973(11)	306(9)	79(5)	
O(B63)	4919(8)	19(8)	124(7)	90(3)	
C(B14)	6939(11)	1493(11)	2078(10)	75(4)	
C(B24)	7656(11)	1785(10)	2926(10)	75(4)	
O(B24)	7325(7)	1437(7)	3604(7)	79(3)	

Table II. (continued)

Atom	x	y	z	U_{eq}	K
C(B34)	8055(10)	2789(10)	3206(9)	65(4)	
O(B34)	8793(7)	3063(7)	4000(7)	75(3)	
C(B44)	8386(11)	3142(10)	2477(10)	75(4)	
C(B54)	7613(12)	2811(11)	1639(10)	81(4)	
O(B44)	8716(6)	4099(6)	2742(6)	70(3)	
O(B54)	7275(8)	1826(8)	1411(8)	90(3)	
C(B64)	7970(2)	3040(2)	852(14)	178(17)	
O(B64)	8670(3)	2750(3)	690(2)	189(18)	0.60
O(B64)	7280(6)	2700(6)	100(6)	250(3)	0.40
C(B15)	9615(11)	4514(11)	2702(10)	77(4)	
C(B25)	10120(11)	5182(10)	3578(10)	71(4)	
O(B25)	10143(7)	4741(7)	4282(7)	77(3)	
C(B35)	9662(10)	5919(9)	3717(9)	61(3)	
O(B35)	10159(7)	6617(7)	4529(6)	75(3)	
C(B45)	9648(11)	6372(10)	2954(10)	70(4)	
C(B55)	9154(12)	5654(11)	2081(10)	80(4)	
O(B45)	9122(7)	7000(7)	3085(7)	75(3)	
O(B55)	9600(7)	4935(7)	2000(7)	75(3)	
C(B65)	9300(2)	6051(15)	1280(11)	129(9)	
O(B65)	10228(17)	6336(13)	1276(13)	166(8)	
C(B16)	9492(11)	7915(10)	3058(10)	72(4)	
C(B26)	9458(11)	8552(11)	3861(10)	75(4)	
O(B26)	9917(8)	8376(8)	4654(7)	87(3)	
C(B36)	8464(10)	8463(10)	3867(10)	70(4)	
O(B36)	8412(7)	9112(7)	4602(7)	79(3)	
C(B46)	7985(10)	8624(10)	3020(10)	71(4)	
C(B56)	8088(12)	8009(12)	2222(11)	83(5)	
O(B46)	7020(7)	8436(6)	2992(6)	72(3)	
O(B56)	9038(8)	8084(8)	2284(8)	90(3)	
C(B66)	7770(2)	8260(2)	1374(14)	148(11)	
O(B66)	8300(3)	9150(3)	1380(2)	233(18)	0.76
O(B66)	7580(7)	7430(8)	640(4)	210(5)	0.24
C(B17)	6597(10)	9163(10)	2910(9)	66(4)	
C(B27)	6126(10)	9262(10)	3654(9)	68(4)	
O(B27)	6763(7)	9568(7)	4497(7)	75(3)	
C(B37)	5417(10)	8427(10)	3545(9)	67(4)	
O(B37)	4926(7)	8539(7)	4226(7)	79(3)	
C(B47)	4753(10)	8164(9)	2647(9)	61(3)	
C(B57)	5233(9)	8087(10)	1930(9)	64(4)	
O(B47)	4142(6)	7264(6)	2520(6)	69(2)	

Table II. (continued)

Atom	x	y	z	U_{eq}	K
O(B57)	5965(7)	8915(7)	2082(6)	71(3)	
C(B67)	4634(14)	7966(12)	1006(10)	91(5)	
O(B67)	4180(8)	8670(8)	998(8)	95(3)	
W(61A1)	7120(3)	1320(2)	9115(16)	139(16)	0.41
W(61A2)	8250(3)	600(3)	520(3)	330(3)	0.74
W(62A1)	340(2)	9488(19)	1566(14)	196(11)	0.84
W(62A2)	1830(10)	9627(9)	9793(9)	106(4)	0.94
W(64A)	20(8)	1840(10)	8520(14)	700(2)	0.35
W(65A)	3316(12)	223(11)	7790(12)	143(5)	
W(67A)	3182(8)	9158(8)	8958(8)	97(3)	0.98
W(21A)	3622(12)	9630(10)	5021(14)	154(7)	0.94
W(22A2)	9060(2)	1177(18)	6030(3)	176(14)	0.61
W(23A)	2217(17)	8940(3)	6298(18)	251(15)	0.95
W(24A)	500(15)	2609(19)	5180(2)	165(12)	0.63
W(26A2)	1510(4)	10180(9)	4250(7)	470(12)	0.39
W(32A)	890(4)	140(4)	5730(5)	160(19)	0.16
W(61B1)	900(3)	3250(3)	9070(3)	370(3)	0.92
W(61B2)	90(2)	4300(3)	414(18)	148(15)	0.45
W(62B1)	2000(2)	1090(2)	8002(15)	209(11)	0.88
W(62B2)	80(2)	1350(2)	9780(3)	203(14)	0.68
W(65B)	1201(12)	8127(11)	1740(11)	144(6)	
W(67B)	2289(9)	8263(8)	581(8)	102(4)	
W(21B)	1820(11)	7830(12)	4528(13)	130(7)	0.80
W(22B)	280(2)	2400(2)	3500(3)	183(16)	0.56
W(23B1)	2530(3)	−751(15)	3261(16)	250(15)	
W(24B)	−1170(19)	919(14)	4280(2)	133(10)	0.59
W(26B2)	1470(5)	−110(3)	5120(6)	280(4)	0.49
W(32B)	1050(5)	620(3)	3340(6)	330(5)	0.50
W(2)	800(4)	820(8)	6480(5)	380(6)	0.59
W(3)	−1010(9)	1050(9)	4950(8)	380(7)	0.50
W(4)	650(10)	2010(9)	7580(5)	420(9)	0.41
O(2A)	5940(3)	5700(4)	8630(3)	392	0.52
O(1A)	7080(4)	5220(4)	9060(3)	405	0.52
C(1A)	6590(3)	5430(3)	8470(2)	484	0.52
C(2A)	6740(3)	5300(3)	7550(2)	372	0.52
C(3A)	6530(3)	6090(3)	7160(2)	449	0.52
C(4A)	6750(3)	6030(3)	6260(2)	483	0.52
C(5A)	6370(3)	5050(3)	5700(2)	544	0.52
C(6A)	5360(3)	4890(3)	5220(2)	425	0.52
C(7A)	5020(4)	4000(3)	4480(3)	425	0.52
C(8A)	5110(4)	4210(3)	3600(2)	388	0.52

Table II. (continued)

Atom	x	y	z	U_{eq}	K
C(9A)	6130(4)	4570(3)	3640(3)	449	0.52
C(10A)	6250(3)	5240(3)	3050(3)	371	0.52
C(11A)	5380(4)	4980(3)	2310(2)	364	0.52
C(12A)	5600(4)	4750(3)	1400(2)	846	0.52
C(13A)	4720(4)	4200(4)	680(2)	491	0.52
O(1B)	6730(5)	5350(4)	540(3)	476	0.48
O(2B)	5340(5)	5280(4)	40(3)	464	0.48
C(1B)	5940(5)	5170(3)	590(3)	501	0.48
C(2B)	5720(4)	4850(3)	1390(2)	270	0.48
C(3B)	6600(4)	4940(4)	2070(3)	470	0.48
C(4B)	6420(3)	5070(3)	2990(3)	594	0.48
C(5B)	7270(3)	5700(4)	3670(3)	433	0.48
C(6B)	7220(3)	5560(4)	4580(3)	561	0.48
C(7B)	6290(3)	4900(3)	4490(2)	592	0.48
C(8B)	6280(3)	4670(3)	5380(3)	497	0.48
C(9B)	6870(3)	5500(3)	6140(2)	500	0.48
C(10B)	6280(3)	5770(3)	6750(2)	577	0.48
C(11B)	6550(3)	5510(3)	7630(2)	352	0.48
C(12B)	7030(4)	6380(3)	8390(2)	358	0.48
C(13B)	7800(3)	6200(5)	9040(3)	399	0.48

ordered and have a minor component pointing inwards (gauche-trans orientation, Figure 2 and Table II).

The β-CD dimers are formed by head-to-head stacking of the β-CD monomers A and B. They are stabilised by means of direct hydrogen bonds between the secondary hydroxyl groups $O(A3n)\cdots O(B3(8-n))$ of mean distance 2.82 Å and range 2.76–2.88 Å.

3.2. DESCRIPTION OF THE GUEST MOLECULES

The aliphatic acids are encapsulated with the carboxyl groups located at one end of the primary hydroxyl side of the β-CD dimer (Figure 1). The guest molecule is disordered over two orientations, *guest A* and *guest B* with approximate occupancy of 50% (*vide supra*). It is assumed that this results from the tendency of the carboxyl groups to self-associate via hydrogen bonds forming the carboxylic dimer. The length of the β-CD dimer is about 15 Å which is shorter than the extended length of aliphatic acids with 13 or 14 carbon atoms. On the other hand the cavity is quite wide, especially in the middle of the dimer and the aliphatic chain forms a bend in

Table III. Positional ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for the β-CD/(Z)-tetradec-7-enoic acid complex (**2**). U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor. Occupancy factors (K) are given when different from one.

Atom	x	y	z	U_{eq}	K
C(A11)	4353(15)	8224(15)	7357(15)	57(3)	
C(A21)	4682(14)	8658(16)	6686(15)	60(3)	
O(A21)	4061(13)	8263(14)	5836(15)	73(2)	
C(A31)	5636(14)	8582(16)	6656(15)	54(3)	
O(A31)	5967(13)	9070(14)	6058(15)	65(2)	
C(A41)	6254(14)	8988(15)	7569(15)	54(3)	
C(A51)	5874(14)	8513(16)	8230(15)	59(3)	
O(A41)	7134(13)	8870(14)	7552(14)	55(2)	
O(A51)	4977(13)	8588(14)	8209(15)	71(2)	
C(A61)	6424(17)	8887(18)	9177(18)	100(5)	
O(A61)	6476(15)	9774(18)	9505(17)	159(7)	
C(A12)	7912(14)	9640(16)	7907(15)	62(3)	
C(A22)	8427(15)	9694(16)	7220(16)	61(3)	
O(A22)	7895(13)	9825(15)	6453(15)	76(2)	
C(A32)	8786(14)	8884(15)	7037(15)	55(3)	
O(A32)	9338(13)	8972(15)	6402(15)	71(2)	
C(A42)	9335(14)	8803(15)	7881(15)	53(3)	
C(A52)	8808(14)	8753(16)	8543(15)	58(3)	
O(A42)	9602(13)	7953(14)	7665(14)	52(2)	
O(A52)	8470(13)	9541(14)	8684(14)	64(2)	
C(A62)	9311(16)	8736(17)	9442(17)	86(4)	
O(A62)	10064(14)	9437(17)	9805(15)	111(4)	
C(A13)	10525(14)	7991(15)	7911(15)	46(2)	
C(A23)	10731(14)	7458(15)	7082(15)	54(3)	
O(A23)	10580(13)	7883(14)	6388(14)	64(2)	
C(A33)	10159(14)	6490(15)	6838(15)	53(3)	
O(A33)	10375(13)	5963(14)	6118(14)	63(2)	
C(A43)	10344(14)	6089(15)	7628(15)	48(2)	
C(A53)	10208(14)	6674(15)	8458(15)	57(3)	
O(A43)	9693(13)	5193(14)	7376(14)	59(2)	
O(A53)	10732(13)	7608(14)	8622(14)	55(2)	
C(A63)	10515(14)	6392(16)	9286(16)	64(3)	
O(A63)	11479(14)	6457(15)	9473(15)	83(3)	
C(A14)	10028(15)	4461(16)	7523(16)	66(3)	
C(A24)	9733(15)	3728(16)	6658(16)	69(3)	
O(A24)	10074(13)	4075(14)	6008(15)	62(2)	
C(A34)	8703(14)	3318(15)	6392(15)	50(3)	

Table III. (continued)

Atom	x	y	z	U_{eq}	K
O(A34)	8435(13)	2592(14)	5589(14)	67(2)	
C(A44)	8378(15)	2990(16)	7119(16)	67(3)	
C(A54)	8692(15)	3754(16)	7946(16)	72(3)	
O(A44)	7406(13)	2651(14)	6857(14)	60(2)	
O(A54)	9675(13)	4102(15)	8191(15)	80(2)	
C(A64)	8441(21)	3466(22)	8738(21)	135(7)	
O(A64)	8769(21)	2747(24)	8899(19)	229(11)	
C(A15)	7007(14)	1761(16)	6900(15)	59(3)	
C(A25)	6312(14)	1256(16)	6023(15)	60(3)	
O(A25)	6770(13)	1229(14)	5312(14)	65(2)	
C(A35)	5570(14)	1704(16)	5860(15)	57(3)	
O(A35)	4891(13)	1217(15)	5061(14)	66(2)	
C(A45)	5130(14)	1736(16)	6642(15)	57(3)	
C(A55)	5842(15)	2187(16)	7512(16)	69(3)	
O(A45)	4501(13)	2257(14)	6508(14)	60(2)	
O(A55)	6569(13)	1766(14)	7595(15)	71(2)	
C(A65)	5469(18)	2089(18)	8312(18)	100(5)	
O(A65)	5167(16)	1154(19)	8306(17)	152(6)	
C(A16)	3577(14)	1865(16)	6541(16)	64(3)	
C(A26)	2952(15)	1937(16)	5718(16)	64(3)	
O(A26)	3120(13)	1464(14)	4928(15)	72(2)	
C(A36)	3039(14)	2922(15)	5723(15)	53(3)	
O(A36)	2402(13)	2980(15)	4977(15)	72(2)	
C(A46)	2857(15)	3410(15)	6579(15)	60(3)	
C(A56)	3484(15)	3295(16)	7388(16)	73(3)	
O(A46)	3057(13)	4359(14)	6604(14)	55(2)	
O(A56)	3405(13)	2329(15)	7305(15)	76(2)	
C(A66)	3242(19)	3615(21)	8228(19)	123(6)	
O(A66)	2298(24)	3060(23)	8156(21)	246(13)	
C(A17)	2357(14)	4795(15)	6694(15)	51(3)	
C(A27)	2232(14)	5267(15)	5953(15)	53(3)	
O(A27)	1940(13)	4616(14)	5104(14)	62(2)	
C(A37)	3082(14)	5976(15)	6048(15)	54(3)	
O(A37)	2960(13)	6464(14)	5372(15)	70(2)	
C(A47)	3339(14)	6630(15)	6945(15)	49(3)	
C(A57)	3416(14)	6152(16)	7682(15)	60(3)	
O(A47)	4246(13)	7255(14)	7072(14)	54(2)	
O(A57)	2586(13)	5410(14)	7513(14)	61(2)	
C(A67)	3544(15)	6759(17)	8605(16)	78(4)	

Table III. (continued)

Atom	x	y	z	U_{eq}	K
O(A67)	2843(14)	7220(15)	8610(15)	89(3)	
C(B11)	3233(14)	7088(16)	2290(15)	57(3)	
C(B21)	2781(14)	6760(15)	2970(15)	58(3)	
O(B21)	3188(13)	7383(14)	3809(15)	73(2)	
C(B31)	2866(14)	5804(15)	2983(15)	53(3)	
O(B31)	2365(13)	5472(14)	3584(15)	67(2)	
C(B41)	2449(14)	5185(16)	2062(15)	58(3)	
C(B51)	2936(15)	5560(15)	1410(15)	59(3)	
O(B41)	2574(13)	4312(14)	2099(14)	54(2)	
O(B51)	2858(13)	6471(15)	1434(15)	70(2)	
C(B61)	2551(17)	5015(18)	467(18)	99(5)	
O(B61)	1665(16)	4964(16)	122(17)	149(6)	
C(B12)	1804(14)	3531(16)	1723(15)	59(3)	
C(B22)	1738(15)	3007(16)	2417(16)	63(3)	
O(B22)	1618(13)	3548(14)	3195(15)	73(2)	
C(B32)	2564(15)	2656(16)	2612(16)	59(3)	
O(B32)	2476(14)	2106(14)	3241(15)	72(2)	
C(B42)	2648(14)	2103(16)	1759(15)	57(3)	
C(B52)	2695(14)	2634(16)	1098(15)	59(3)	
O(B42)	3489(13)	1845(14)	1977(14)	52(2)	
O(B52)	1910(13)	2970(14)	955(14)	65(2)	
C(B62)	2711(16)	2126(17)	203(16)	83(4)	
O(B62)	1997(16)	1376(15)	−165(15)	115(4)	
C(B13)	3449(14)	919(15)	1738(15)	48(2)	
C(B23)	3976(14)	707(15)	2556(15)	54(3)	
O(B23)	3560(13)	867(15)	3260(14)	69(2)	
C(B33)	4952(14)	1295(15)	2808(15)	53(3)	
O(B33)	5479(13)	1070(15)	3526(14)	65(2)	
C(B43)	5355(14)	1101(15)	2017(15)	50(3)	
C(B53)	4779(14)	1229(15)	1184(15)	56(3)	
O(B43)	6252(13)	1754(14)	2269(14)	p61(2)	
O(B53)	3841(13)	710(14)	1019(14)	55(2)	
C(B63)	5044(15)	920(16)	363(16)	67(3)	
O(B63)	4986(14)	−42(15)	175(15)	86(3)	
C(B14)	6988(15)	1421(16)	2113(16)	65(3)	
C(B24)	7717(15)	1709(16)	2978(16)	64(3)	
O(B24)	7370(13)	1378(14)	3640(15)	65(2)	
C(B34)	8119(14)	2739(15)	3254(15)	51(3)	
O(B34)	8855(13)	3012(14)	4050(15)	67(2)	
C(B44)	8457(15)	3062(16)	2520(16)	64(3)	
C(B54)	7691(15)	2749(16)	1697(16)	72(3)	

Table III. (continued)

Atom	x	y	z	U_{eq}	K
O(B44)	8785(13)	4040(14)	2785(14)	59(2)	
O(B54)	7333(14)	1763(15)	1448(15)	79(2)	
C(B64)	7966(19)	3023(21)	895(20)	124(6)	
O(B64)	8693(23)	2669(23)	738(19)	227(11)	
C(B15)	9672(14)	4446(16)	2742(15)	59(3)	
O(B25)	10216(13)	4675(14)	4330(15)	65(2)	
C(B25)	10176(14)	5123(16)	3615(15)	61(3)	
C(B35)	9727(14)	5873(16)	3778(15)	57(3)	
O(B35)	10232(13)	6558(14)	4581(14)	68(2)	
C(B45)	9710(14)	6311(15)	3004(15)	57(3)	
C(B55)	9235(15)	5593(16)	2120(16)	64(3)	
O(B45)	9185(13)	6940(14)	3136(14)	62(2)	
O(B55)	9668(13)	4877(15)	2046(15)	71(2)	
C(B65)	9347(17)	5979(19)	1342(18)	102(5)	
O(B65)	10297(18)	6270(17)	1341(17)	158(6)	
C(B16)	9574(15)	7863(16)	3097(16)	62(3)	
C(B26)	9496(15)	8480(16)	3931(16)	65(3)	
O(B26)	9979(13)	8318(15)	4715(15)	73(2)	
C(B36)	8516(14)	8409(15)	3916(15)	55(3)	
O(B36)	8462(13)	9036(15)	4667(15)	74(2)	
C(B46)	8043(14)	8588(16)	3073(15)	57(3)	
C(B56)	8146(15)	7964(16)	2252(16)	71(3)	
O(B46)	7088(13)	8391(14)	3037(14)	55(2)	
O(B56)	9112(13)	8029(15)	2348(15)	76(2)	
C(B66)	7818(19)	8208(20)	1425(19)	116(6)	
O(B66)	8367(24)	9143(26)	1492(22)	257(14)	
C(B17)	6647(14)	9086(15)	2952(15)	50(3)	
C(B27)	6189(14)	9211(15)	3703(15)	53(3)	
O(B27)	6824(13)	9505(14)	4534(14)	64(2)	
C(B37)	5467(14)	8360(15)	3597(15)	56(3)	
O(B37)	4974(13)	8477(15)	4280(14)	69(2)	
C(B47)	4798(14)	8087(15)	2688(15)	49(3)	
C(B57)	5291(14)	8036(15)	1961(15)	57(3)	
O(B47)	4187(13)	7206(14)	2573(14)	54(2)	
O(B57)	6031(13)	8859(14)	2136(14)	61(2)	
C(B67)	4698(16)	7908(17)	1042(16)	77(4)	
O(B67)	4233(14)	8605(15)	1040(15)	91(3)	
W(61A1)	7266(32)	11305(24)	9184(22)	31(13)	0.40
W(61A2)	8339(30)	567(29)	518(30)	145(16)	0.35

Table III. (continued)

Atom	x	y	z	U_{eq}	K
W(62A1)	417(25)	9413(24)	1594(20)	133(9)	0.52
W(62A2)	1889(14)	9555(15)	9821(15)	96(3)	
W(64A)	−54(71)	2013(73)	8349(67)	122(30)	0.13
W(65A)	3351(16)	152(17)	7813(17)	109(4)	0.80
W(67A)	3256(14)	9104(15)	9029(15)	88(3)	
W(21A1)	3663(16)	9551(16)	5059(18)	149(6)	
W(21A2)	9251(44)	1225(30)	6286(29)	105(20)	0.26
W(22A)	8998(26)	1002(28)	5754(35)	91(11)	0.31
W(23A)	2277(19)	−1152(25)	6341(22)	161(12)	0.59
W(24A)	562(17)	2580(21)	5274(24)	131(10)	0.51
W(26A1)	1463(41)	426(41)	3926(41)	114(17)	0.25
W(26A2)	1668(44)	−156(46)	4472(45)	167(19)	0.31
W(32A)	800(28)	321(28)	6202(37)	92(12)	0.26
W(61B1)	903(25)	3122(26)	9119(30)	149(16)	0.39
W(61B2)	10135(22)	4175(36)	10458(22)	145(15)	0.41
W(62B1)	2007(23)	1001(26)	8029(19)	146(10)	0.57
W(62B2)	10110(24)	1336(25)	−180(30)	134(14)	0.37
W(64B)	9445(71)	1464(73)	1385(65)	203(35)	0.24
W(65B)	1286(15)	8078(17)	1826(16)	113(4)	0.85
W(67B)	2332(14)	8180(15)	612(15)	86(3)	
W(21B)	1894(15)	7782(17)	4580(18)	104(5)	0.70
W(22B)	341(21)	2336(24)	3627(32)	132(14)	0.39
W(23B1)	2761(30)	9136(26)	3202(30)	113(13)	0.40
W(23B2)	12350(42)	9223(42)	3477(32)	107(17)	0.27
W(24B)	8876(19)	885(18)	4348(24)	123(10)	0.50
W(26B1)	1049(37)	−38(39)	5732(37)	91(14)	0.23
W(26B2)	1570(46)	−244(47)	5195(47)	132(19)	0.23
W(32B)	11174(30)	629(35)	3411(39)	114(14)	0.28
W(1)	360(64)	588(60)	3091(56)	128(24)	0.17
W(2)	807(64)	1027(74)	6537(62)	113(26)	0.14
O(1A)	5880	4260	60	858	0.51
O(2A)	5230	5290	300	605	0.51
C(1A)	5510	4680	530	411	0.51
C(2A)	5380	4450	1390	596	0.51
C(3A)	6250	5000	2100	442	0.51
C(4A)	6030	5310	2980	702	0.51
C(5A)	6830	5290	3710	727	0.51
C(6A)	6600	4370	3940	762	0.51

Table III. (continued)

Atom	x	y	z	U_{eq}	K
C(7A)	5590	4110	3950	918	0.51
C(8A)	5370	4210	4720	503	0.51
C(9A)	6070	4210	5550	845	0.51
C(10A)	6490	5220	6120	605	0.51
C(11A)	6130	5340	6940	721	0.51
C(12A)	6890	5440	7780	441	0.51
C(13A)	7010	6320	8480	304	0.51
C(14A)	7820	6460	9290	453	0.51
O(1B)	7000	5520	9530	756	0.49
O(2B)	6020	6230	9260	573	0.49
C(1B)	6680	5990	9100	573	0.49
C(2B)	7110	6310	8400	1021	0.49
C(3B)	6990	5470	7650	426	0.49
C(4B)	6250	5450	6830	467	0.49
C(5B)	6360	4840	6010	751	0.49
C(6B)	7350	5110	5950	561	0.49
C(7B)	7570	6060	5760	749	0.49
C(8B)	7470	6120	4930	334	0.49
C(9B)	7090	5240	4170	747	0.49
C(10B)	7070	5460	3260	470	0.49
C(11B)	6080	5290	2750	696	0.49
C(12B)	5850	4490	1910	452	0.49
C(13B)	5190	4630	1150	487	0.49
C(14B)	5320	4200	260	915	0.49

that region in both complexes. The aliphatic chain is quite labile inside the cavity, a fact reflected in the thermal parameters of the guest atoms which are considerably higher than those of the host.

In the tridecanoic acid complex both orientations of the guest have the bend towards the same direction, the *guest A* orientation being more curled within the cavity. The carboxyl group of *guest A* orientation is located 2.8 Å above the mean plane of the glucosidic oxygen atoms O(4n) while that of the *guest B* orientation is located 3.6 Å above the corresponding mean plane of O(4n) atoms and comes within H-bond distance of the carboxyl group of *guest A* of the adjacent β-CD dimer along the channel (Figure 3, Table Va). In addition, the *guest B* orientation comes within H-bonding distance to the inwards pointing atom O(A66b) (gauche-trans orientation) of the β-CD host above (O(2B)$\cdots$O(A66b) distance 2.84 Å). In *guest B* orientation the combination of the bending of the aliphatic chain and its

Table IV. β-Cyclodextrin macrocycle characteristics.

Residue		D^a (Å)	φ^b (°)	d^c (Å)	α^d (°)	D_3^e (Å)
β-CD/tridecanoic acid						
G1	mol A	4.38	130	0.018(7)	11.2(3)	2.85
	mol B	4.40	130	−0.020(7)	9.9(3)	2.84
G2	mol A	4.29	126	−0.033(7)	14.5(2)	2.87
	mol B	4.30	125	0.031(7)	13.2(2)	2.88
G3	mol A	4.49	128	0.008(7)	9.6(2)	2.87
	mol B	4.45	129	−0.005(7)	9.8(2)	2.89
G4	mol A	4.32	131	0.020(7)	13.5(4)	2.88
	mol B	4.34	131	−0.017(7)	14.4(4)	2.85
G5	mol A	4.37	128	−0.011(7)	12.1(5)	2.89
	mol B	4.40	127	0.003(7)	12.4(5)	2.84
G6	mol A	4.34	127	−0.017(7)	10.4(5)	2.80
	mol B	4.29	127	0.022(7)	10.4(5)	2.82
G7	mol A	4.45	130	0.014(7)	6.0(3)	2.80
	mol B	4.46	130	−0.013(7)	5.5(3)	2.78
β-CD/(Z)-tetradec-7-enoic acid						
G1	mol A	4.41	130	0.016(5)	10.4(2)	2.86
	mol B	4.39	130	−0.010(5)	11.0(2)	2.84
G2	mol A	4.28	126	−0.027(5)	13.0(2)	2.87
	mol B	4.28	126	0.021(5)	14.1(2)	2.86
G3	mol A	4.48	129	0.007(6)	9.3(1)	2.84
	mol B	4.46	129	−0.007(6)	9.0(2)	2.84
G4	mol A	4.33	131	0.014(6)	13.6(3)	2.84
	mol B	4.33	131	−0.014(6)	13.9(3)	2.83
G5	mol A	4.39	127	0.007(6)	12.6(4)	2.86
	mol B	4.40	127	0.011(6)	12.5(4)	2.84
G6	mol A	4.32	127	−0.012(5)	10.9(4)	2.80
	mol B	4.32	127	0.008(5)	10.8(4)	2.80
G7	mol A	4.44	130	0.009(5)	6.0(2)	2.79
	mol B	4.46	130	−0.010(5)	6.1(3)	2.77

[a] Distances between atoms $O(4n) \cdots O(4(n+1))$.
[b] Angles between atoms $O(4(n-1)) \cdots O(4n) \cdots O(4(n+1))$.
[c] Deviations (Å) from the least-squares optimum plane of the seven $O(4n)$ atoms.
[d] Tilt angle between the $O(4n)$ plane and optimum planes through $O(4(n-1))$, $C(1n)$, $C(4n)$ and $O(4n)$.
[e] Intramolecular hydrogen-bond distances between atoms $O(3n) \cdots O(2(n+1))$.

Table V. Hydrogen bonds of β-CD/tridecanoic acid (**1**) and β-CD/(*Z*)-tetradec-7-enoic acid (**2**) complexes.

a. *Hydrogen bonds between guest's carboxyl groups*

Complex	Distance (Å)	Angles (°) [C(1A)–O(nA)···O(nB)]	Angles (°) [O(nA)···O(nB)–C(1B)]
β-CD/tridecanoic acid			
O(1A)···O(1B)	2.50	119	121
O(2A)···O(2B)	2.74	117	112
β-C D/(Z)-tetradec-7-enoic acid			
O(1A)···O(1B)	2.70	106	120
O(2A)···O(2B)	2.71	121	112

slight translation towards the exterior results in the terminal methyl group entering inside the cavity more than in the *guest A* orientation. The distance between two neighbouring methyl groups is 6.4 Å.

The β-CD/(*Z*)-tetradec-7-enoic acid complex has the same overall shape. However, the bend due to the *cis* double bond between the C(7) and C(8) carbon atoms is directed towards diametrically opposite directions. The carboxyl oxygen atoms of the two orientations of the guest molecule protrude from the cavity to the same extent (mean distance from the O(4n) plane 3.6 Å for both *guest A* and *guest B*) and two adjacent carboxyl groups also form carboxylic dimers (Table Va). The terminal methyl group located at the other primary side has a distance of 5.3 Å from the methyl group of the next dimer along the channel.

3.3. SUPRAMOLECULAR ORGANISATION

In the β-CD/tridecanoic acid complex 19.5 water molecules have been located distributed over 28 sites, while in β-CD/(*Z*)-tetradec-7-enoic acid 14.9 water molecules are distributed over 32 sites. Most of the water molecules are H-bonded to hydroxyl groups of the host and they are labelled by the nearest hydroxyl group to which they are H-bonded. There is a great homology of almost all the water molecules of both complexes to the other dimeric inclusion complexes of β-CD [5] and great attention has been paid to the systematic labelling of the water molecules in order to be in accordance with all the previously published isomorphous structures. In Table Vb, distances and angles of the hydrogen bonds between the hydroxyl groups and the water molecules in the range 2.40–3.20 Å are listed. It is noteworthy that there exist two separate water networks [14] one connecting the primary hydroxyl side and another the secondary (Table Vb).

β-CD dimers form semi-invariant 2-D layers of real or pseudo $C2$ symmetry [5, 14] irrespective of the guest, by hydrogen bond formation either directly

Table V. (continued)

b. *Hydrogen-bonds between β-CD dimers and water moelcules.*

Molecule A	Complex **1**		Complex **2**		Molecule B	Complex **1**		Complex **2**	
	D	A	D	A		D	A	D	A
O(A21)$\cdots$W(21A$_1$)	2.71	111	2.69	111	O(B21)$\cdots$W(21B)	2.71	111	2.70	110
O(A22)$\cdots$W(22A)	2.71	101	2.77	108	O(B22)$\cdots$W(22B)	2.68	100	2.71	102
$\cdots$W(21A$_2$)	–		2.76	95					
O(A23)$\cdots$W(23A)	2.75	108	2.75	106	O(B23)$\cdots$W(23B$_1$)	2.74	106	2.67	99
					$\cdots$W(23B$_2$)	–		2.94	114
O(A24)$\cdots$W(24A)	2.80	97	2.74	97	O(B24)$\cdots$W(24B)	2.76	97	2.75	96
O(A26)$\cdots$W(26A$_2$)	2.66	102	2.82	100	O(B26)$\cdots$W(26B$_2$)	2.82	97	2.78	101
$\cdots$W(26A$_1$)	–		2.68	105	$\cdots$W(32A)	2.83	103	–	
					$\cdots$W(26B$_1$)	–		2.69	106
O(A32)$\cdots$W(2)	3.19	124	–		O(B32)$\cdots$W(32B)	2.91	138	2.79	137
$\cdots$W(32A)	3.19	151	2.84	137					
O(A34)$\cdots$W(22A)	2.91	108	2.86	115	O(B34)$\cdots$W(22B)	2.94	107	2.91	108
$\cdots$W(3)	2.92	137	–						
$\cdots$W(21A$_2$)	–		3.01	100					
O(A35)$\cdots$W(21A$_1$)	2.81	120	2.84	118	O(B35)$\cdots$W(21B)	2.84	118	2.84	118
O(A36)$\cdots$W(24A)	2.93	110	2.95	110	O(B36)$\cdots$W(3)	2.85	128	–	
					$\cdots$W(24B)	2.92	110	2.98	108
O(A61)$\cdots$W(61A$_1$)	2.61	131	2.62	134	O(B61)$\cdots$W(61B$_2$)	2.62	134	2.62	132
$\cdots$W(61A$_2$)	2.87	103	2.87	111	$\cdots$W(61B$_1$)	2.77	103	2.84	103
O(A62)$\cdots$W(62A$_2$)	2.81	131	2.81	130	O(B62)$\cdots$W(62A$_2$)	2.79	129	2.81	129
$\cdots$W(62A$_1$)	2.81	104	2.80	102	$\cdots$W(62B$_1$)	2.80	100	2.82	103
$\cdots$W(62B$_2$)	2.90	123	2.95	123	$\cdots$W(62B$_2$)	2.89	125	2.93	124
O(A63)$\cdots$W(67B)	2.81	104	2.78	104	O(B63)$\cdots$W(67A)	2.81	106	2.79	104
O(A64a)$\cdots$W(64A)	3.03	140	2.59	134	O(B64)$\cdots$W(64B)	–		2.71	133
$\cdots$W(61B$_2$)	3.04	86	3.02	84	$\cdots$W(61B$_2$)	3.06	109	3.02	108
$\cdots$W(61A$_1$)	3.13	113	3.18	114	$\cdots$W(61A$_1$)	3.15	82	3.01	85
					$\cdots$W(61A$_2$)	–		3.14	116
O(A65a)$\cdots$W(61A$_1$)	2.82	103	–			–	–	–	
O(A65b)$\cdots$W(65A)	2.77	124	2.76	124	O(B65)$\cdots$W(65B)	2.73	122	2.75	122
$\cdots$W(61A$_1$)	3.09	90	3.23	88	$\cdots$W(61B$_2$)	3.14	89	3.22	88
O(A66a)$\cdots$W(4)	2.61	158	–		O(B66)$\cdots$W(61A$_2$)	2.88	142	2.96	139
$\cdots$W(61B$_1$)	2.83	142	2.92	138	$\cdots$W(62A$_1$)	3.05	118	3.10	116
$\cdots$W(62B$_1$)	3.11	116	3.10	117					
O(A66b)$\cdots$O(2B)	2.84	134	–		O(B66)$\cdots$O(1B)	3.17	130	–	
O(A67)$\cdots$W(67A)	2.76	123	2.77	122	O(B67)$\cdots$W(67B)	2.79	122	2.80	122

D: Distance (Å) O(Aor B*mn*)$\cdots$W(*mn*A or B), A: Angle (°) C(A or B*mn*)–O(A or B*mn*)$\cdots$W(*mn*A or B).

Table V. (continued)

c. *Direct Hydrogen-bonds between dimers*

O(mn)$\cdots$O(mn')	Distance (Å) O(mn)$\cdots$O(mn')		Angle (°) C(mn)–O(mn)$\cdots$O(mn')		Angle (°) O(mn)$\cdots$O(mn')–C(mn')	
	1	**2**	**1**	**2**	**1**	**2**
O(A25)$\cdots$O(B27) (i)	2.77	2.76	114	114	107	107
O(A27)$\cdots$O(B25) (ii)	2.80	2.76	105	106	113	114
O(A63)$\cdots$O(A67) (iii)	2.89	2.91	130	130	113	113
O(B63)$\cdots$O(B67) (iv)	2.90	2.90	131	129	114	113
O(A63)$\cdots$O(B61) (v)	2.76	2.78	105	106	112	113
O(A61)$\cdots$O(B63) (vi)	2.77	2.80	116	112	105	106
O(A64)$\cdots$O(B64) (vii)	2.93	2.98	114	107	104	106

Translation operators: (i) $x, 1 - y, z$, (ii) $1 - x, y, z$, (iii) $1 + x, y, z$, (iv) $x, 1 - y, z$, (v) $1 + x, y, 1 + z$, (vi) $x, 1 + y, 1 + z$, (vii) $x, y, 1 + z$.

through the primary and secondary hydroxyl groups or via water molecules. The direct H-bonding interactions of the β-CD hydroxyl oxygen atoms of the same 2-D layer within 2.40–3.20 Å are shown in Table Vc. Those are between the O(A25)$\cdots$O(B27) and O(A27)$\cdots$O(B25) hydroxyl groups of the secondary side and the O(A63)$\cdots$O(A67) and O(B63)$\cdots$O(B67) hydroxyl groups of the primary side.

The 3-D lattice is formed by alignment of the 2-D layers in such way that the mean angle between the dimer axis and the c crystallographic axis is 9°. The mean distance of the centre of mass of two consecutive dimers as projected onto the O4n mean plane is 2.5 Å so each dimer aligns almost on top of the dimer below to form a channel (Figure 1). There is one strong direct H-bond between the outward pointing primary oxygen atoms O(A64a)$\cdots$O(B64a) (gauche-gauche conformation), along each channel (Table Vc).

Moreover, direct hydrogen bonds between O(A61)$\cdots$O(B63) and O(A63)$\cdots$O(B61) of neighbouring 2-D layers lying on the planes [b, c] and [a, c], respectively, connect the channels between layers and lead to higher level organisation, i.e., interactions between channels (Figure 3). The above interactions are reinforced by the H-bonds of the interconnecting water molecules among the β-CD dimers as mentioned above (Table Vb).

The 3-D lattice of the dimeric complexes of β-CD is formed by alignment of the 2-D layers in four different ways [5, 15]. The selection of the guest is crucial to the relative positioning of the dimeric complexes. Hydrophilic H-bonding groups of the guest at the primary faces of the β-CD favour extensive hydration. In contrast, hydrophobic groups at the primary faces favour protection of the guest from the aqueous environment, thus giving channel packing which is the least hydrated. In the present structures the guest is amphiphilic. The two terminal groups, the carboxyl and methyl groups, are located at the two opposite primary faces of the β-CD dimer. We believe that the presence of the methyl group at one end is

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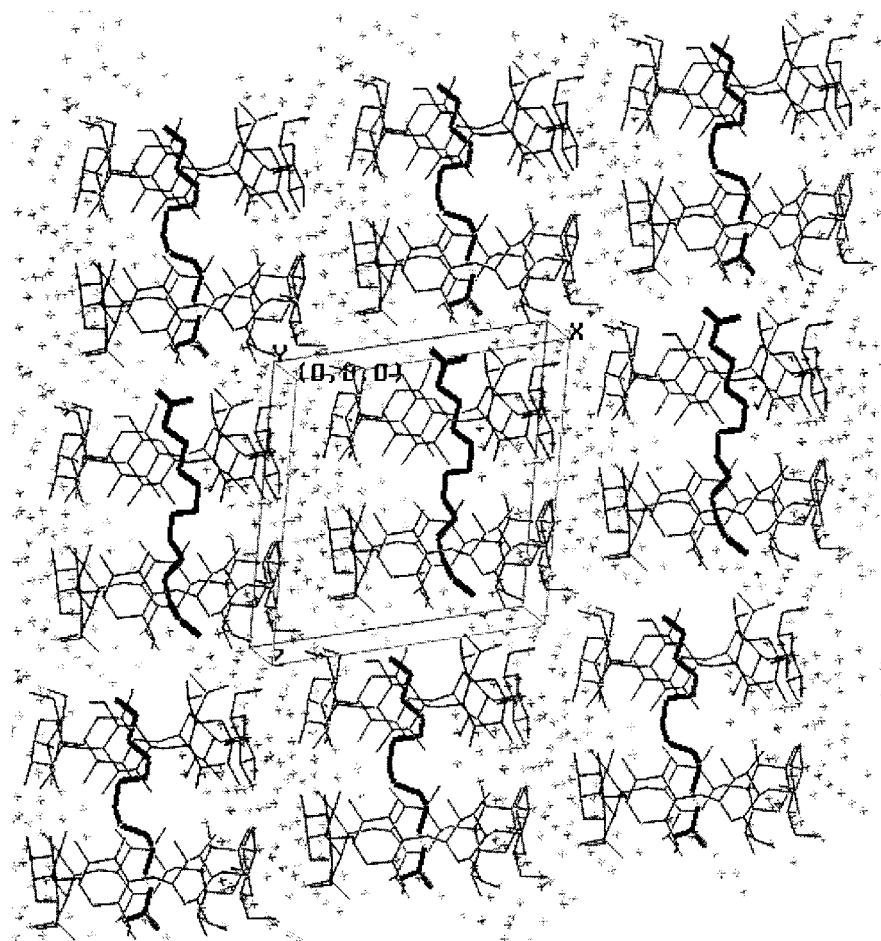
Figure 3. The supramolecular arrays of the β-CD/tridecanoic acid complex. The guest molecules are shown in bold. The water molecules surround the channels but do not enter inside them.

directing the packing towards formation of channels that are hydrophobic and do not allow any water molecules to enter. Otherwise, the methyl group would be exposed to the aqueous environment present at the exterior of the dimer. At the opposite end, the carboxyl groups of two adjacent dimers come close and become stabilised by forming a carboxylic dimer inside the channel. Determinations of the unit cells of inclusion complexes of β-CD with aliphatic monocarboxylic acids with 13–16 carbon atoms [8] showed that they are isomorphous with the complexes reported here, they also form [3]pseudorotaxanes and pack in channels. In contrast, structures of inclusion complexes of β-CD with aliphatic α,ω-dicarboxylic acids with 10–16 carbon atoms [8] have shown that the β-CD dimers do not align in channels. The carboxyl groups at the two opposite faces of the dimers are hydrated

and do not H-bond directly to adjacent carboxyl groups. Therefore, in the case of the monocarboxylic acids with 13–16 carbon atoms we conclude that the driving force for the channel formation is the need of the terminal methyl group to be protected from the aqueous environment as well as the ability of the carboxyl group to form a stable synthon, the carboxylic dimer, that overall behaves like a non-polar entity [16] and can be accommodated in the hydrophobic channel.

Acknowledgments

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