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Note

Crystal structure of cyclomaltoheptaose (β-cyclodextrin) complexes with *p*-aminobenzoic acid and *o*-aminobenzoic acid

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ABSTRACT

Crystal structures of cyclomaltoheptaose (β-cyclodextrin) complexes with *p*-aminobenzoic acid and *o*-aminobenzoic acid have been determined by single-crystal X-ray diffraction. The space group of the β-cyclodextrin–*p*-aminobenzoic acid complex is $P2_1$ with a host:guest stoichiometry of 1:1, and that of the β-cyclodextrin–*o*-aminobenzoic acid complex is *P*1 with a stoichiometry of 2:3. The different structures of the guest molecules lead to the different molecular packing structures of the two complexes. Intermolecular hydrogen-bond interactions are the main force that stabilize the supramolecular systems. In both crystals, there are water molecules located near the cavity rims and in interstices between molecules of β-cyclodextrin participating in formation of intermolecular hydrogen bonds.

Cyclomaltoheptaose (β-cyclodextrin, β-CD) is a macrocyclic oligosaccharide consisting of seven α-(1→4)-linked D-glucose units.[1] It forms a torus-like macrocycle with the primary 6-OH groups on the narrow side and the secondary 2-OH and 3-OH hydroxyl groups at the wide side.[2] CDs are well known for their ability to form inclusion complexes with a variety of guest molecules fitting partially or completely into the host CD cavity as shown by crystallographic results.[3–5] Several factors are recognized to be responsible for the formation of inclusion complexes of cyclodextrins (CDs) with suitable guest molecules: van der Waals forces, and hydrogen bonds, as well as hydrophobic and dipole–dipole interactions.[6] Single-crystal X-ray diffraction studies of host–guest (H–G) complexes of CDs provide detailed information on the role of such weak interactions for establishing host–guest supramolecular assemblies,[7] molecular recognition, and stereodifferentiation.[6,8]

In this work, in order to understand how the nature of the guest molecule determines the host–guest ratio and the crystal packing, we have carried out an investigation of *p*-aminobenzoic acid and *o*-aminobenzoic acid as guest molecules. The structures of the host and guest molecules are given in Figure 1: Gn denotes the *n*th glucosidic residue of the β-CD.

Structure of the inclusion complexes: In the β-CD–*p*-aminobenzoic acid complex, β-CD forms a 1:1 complex with *p*-aminobenzoic acid as shown in Figure 2a. β-CD and *o*-aminobenzoic acid form a 2:3 host–guest inclusion complex (Fig. 2b). Two crystallographically independent β-CD molecules per unit cell form head-to-head dimers by means of intermolecular hydrogen bonds.

Structure description of β-CD: All glucose residues are in the normal $^4C_1$ chair conformation, and the overall β-cyclodextrin molecule has an approximate 7-fold axis. The geometric parameters for the β-CD molecules are listed in Table 1.

The glycosidic O4*n* atoms lie in a plane within 0.28 Å, the O4*n*···O4(*n* + 1) distances vary between 4.235 and 4.494 Å, and the values of the angles between the glucosidic oxygen atoms O4(*n* − 1)···O4*n*···O4(*n* + 1) do not differ significantly from 128.57° (between 124.47° and 130.42°), the ideal value for an angle of a regular heptagon, denoting that the cavity is only slightly distorted due to inclusion. The annular shape of the β-CD is stabilized by the interglucose hydrogen bonds connecting the secondary hydroxyl groups O3*n* and O2(*n* + 1) of neighboring glucosidic units (Table 1) (average O3*n*···O2(*n* + 1) distance 2.864 Å, range 2.773–2.951 Å) similar to other β-CD complexes.[2,5,9,10] The orientation of the C6–O6 bond is described by torsion angles C4*n*–C5*n*–C6*n*–O6*n* and O5*n*–C5*n*–C6*n*–O6*n*, listed in Table 1. Most of the primary hydroxyl groups (major disordered sites) have the *gauche–gauche* orientation (mean torsion angles C4*n*–C5*n*–C6*n*–O6*n* and O5*n*–C5*n*–C6*n*–O6*n* 55.00 and −66.41°, respectively) and point out of the cavity, except for glucose residue G6 (labeled in Fig. 2a), where a *gauche–trans* orientation is adopted and O-6 points toward the cavity. Five water molecules are disposed outside the cavity at borders of the toroid rims and in interstices between β-CD molecules. Table 2 lists the hydrogen bonds of the β-CD A with the guest and water molecules.

Table 1 lists the geometrical parameters for the two independent β-CD molecules B and C that comprise the complex. Average bond lengths and angles of B and C show that the monomers have similar geometries which compares well with other β-CD

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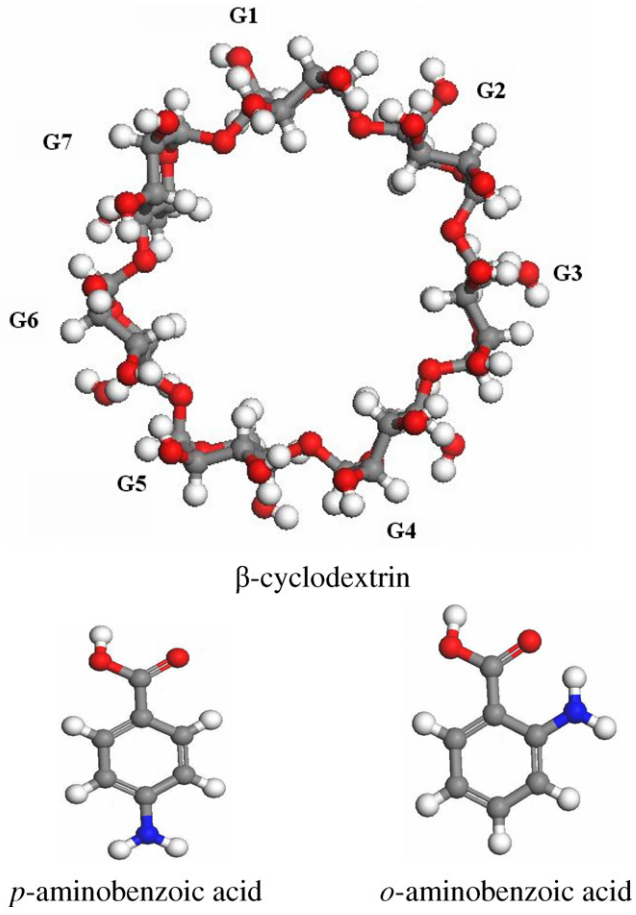

Figure 1. The structures of β-cyclodextrin, *p*-aminobenzoic acid and *o*-aminobenzoic acid.

complexes.[11,12] All O6*n*–C6*n* bonds of molecule B are directed away from the macrocyclic cavity, adopting the *gauche–gauche* conformation (mean torsion angles C4*n*–C5*n*–C6*n*–O6*n* and O5*n*–C5*n*–C6*n*–O6*n* 56.72° and −63.67°, respectively). However, the O6*n*–C6*n* bonds within the glucose residue G7 of molecule C (labeled in Fig. 2b) adopt a *gauche–trans* orientation and point toward of the cavity. All the other primary hydroxyl groups are in the *gauche–gauche* orientation with the mean torsion angles C4*n*–C5*n*–C6*n*–O6*n* and O5*n*–C5*n*–C6*n*–O6*n* at 57.64° and −62.68°, respectively.

The two β-CDs B and C form a head-to-head dimer in which the two O-4 planes make an angle of 20.10° and the corresponding distance from center to center of the two O-4 planes is 7.084 Å. The glycosidic O4*n* atoms of β-CD B lie in a plane within 0.03 Å, the O4*n*···O4(*n* + 1) distance varies between 4.282 and 4.423 Å, and the O4(*n* − 1)···O4*n*···O4(*n* + 1) angles range from 125.35° to 131.52°. This gives the cavity a slightly elliptical shape that could be related to the shape of the guest molecule. Hydrogen bonds O3*n*-H···O2(*n* + 1) between neighboring glucose residue (2.698–2.775 Å; Table 1) stabilize and maintain the rigidity and 'roundness' of β-CD B.

As shown in Table 1, the β-CD molecule C also possesses a near-sevenfold symmetry. The maximal deviation of the O4*n* atoms to their least-squares plane is less than 0.02 Å. The distances O4*n*···O4(*n* + 1) range from 4.272 to 4.497 Å, and the angles O4(*n* − 1)···O4*n*···O4(*n* + 1) range from 122.62° to134.87°. The annular geometry of β-CD C is stabilized by interglucose O3*n*–H···O2(*n* + 1) hydrogen bonds with O···O distances 2.703–2.803 Å. There are 23 water molecules per asymmetric unit, distributed over 28 sites. All the hydrogen bonds between the two β-CDs molecules B and C and of the two β-CDs with the guest molecule and water molecules are listed in Table 3.

Geometry of the guest molecule: In the β-CD–*p*-aminobenzoic acid complex, the guest molecule is deeply included into the cavity of the β-CD, with the amino group located on the wide site of the cavity and the carboxyl at the narrow side as shown in Figure 2a. Its molecular plane makes an angle of 72.30° with the O-4 plane made by the seven O4*n* atoms of the β-CD, and the mass center of the aromatic ring is 1.643 Å below the mass center of the O-4 plane.

Host–guest interaction plays a crucial role in determining the orientation of a guest molecule in the cavity.[13] There is no conventional hydrogen bond observed between β-CD and its guest mole-

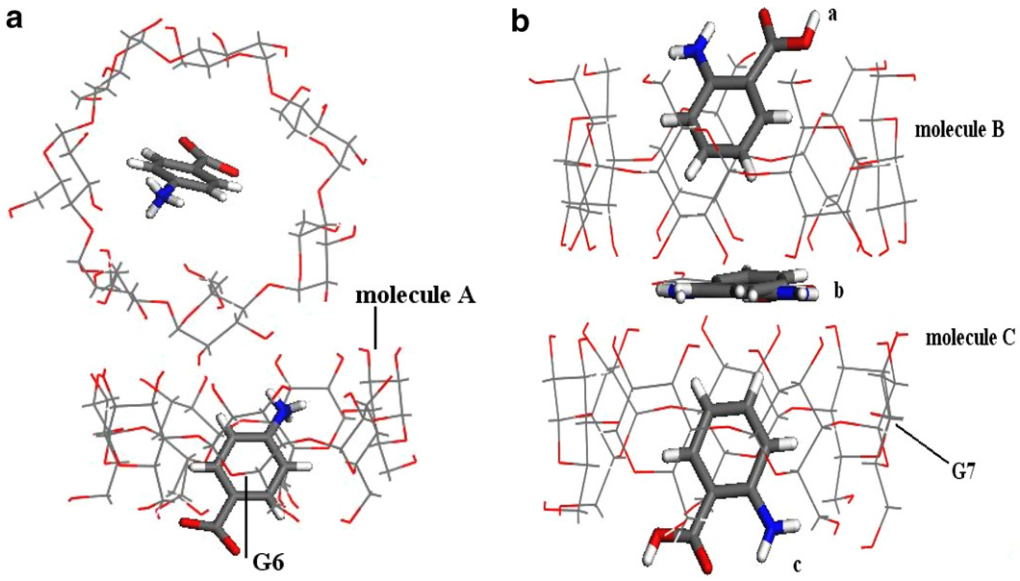

Figure 2. (a) X-ray structure of the 1:1 host–guest inclusion complex between β-CD and *p*-aminobenzoic acid. (b) The crystal structure of the 2:3 host–guest inclusion complex between β-CD and *o*-aminobenzoic acid.

Table 1
β-CD macrocycle characteristics

Residue	D^a (Å)	φ^b (°)	d^c (Å)	D^d (Å)	Torsion angle (°) C4*n*–C5*n*–C6*n*–O6*n*	O5*n*–C5*n*–C6*n*–O6*n*
Molecule A						
G1	4.494	130.42	0.18	2.951	55.58 (−158.13)	−68.23 (89.34)
G2	4.410	129.82	−0.16	2.877	49.51 (179.22)	−71.69 (61.60)
G3	4.263	127.53	−0.10	2.887	60.22	−60.55
G4	4.403	124.63	0.21	2.804	57.26	−63.59
G5	4.480	133.19	0.05	2.773	51.67	−69.85
G6	4.235	128.60	−0.28	2.879	−178.58	61.86
G7	4.307	124.47	0.10	2.886	55.75	−64.56
Molecule B						
G1	4.331	128.97	0.01	2.724	61.64	−59.20
G2	4.282	125.35	−0.01	2.775	53.64	−67.94
G3	4.423	129.88	−0.02	2.759	53.21	−65.95
G4	4.351	131.52	0.03	2.770	53.37	−66.80
G5	4.290	125.49	0.00	2.698	57.24	−62.53
G6	4.366	128.02	−0.03	2.706	56.57	−65.19
G7	4.420	130.73	0.02	2.752	61.38	−58.05
Molecule C						
G1	4.310	122.62	−0.01	2.803	54.57	−66.43
G2	4.497	132.57	0.02	2.787	57.85	−61.56
G3	4.331	132.04	−0.01	2.802	54.59	−67.27
G4	4.272	123.79	0.00	2.746	57.24	−61.96
G5	4.369	126.71	0.00	2.703	56.67	−64.78
G6	4.483	134.87	0.02	2.771	64.92	−54.08
G7	4.281	127.38	−0.01	2.792	−175.94	63.27

[a] Distance between atoms O4*n*···O4(*n* + 1).
[b] Angles between atoms O4(*n* − 1)···O4*n*···O4(*n* + 1).
[c] Deviations (Å) from the least-squares optimum plane of the seven O4*n* atoms.
[d] Intramolecular hydrogen-bond distance between O3*n*···O2(*n* + 1).

Table 2
Hydrogen bonds of the β-CD A with the guest molecule and water molecules

D–H	*d*(H···A) (Å)	∠DHA (°)	*d*(D···A) (Å)	*A*
Between β-CD and water molecules				
O17–H17	1.985	153.50	2.743	O38W [−*x* + 1, *y* + 1/2, −*z* + 1]
O25–H25	2.006	163.45	2.801	O40W [−*x* + 1, *y* + 11/2, *z* + 1]
O27–H27	2.317	115.99	2.776	O41W [*x*, *y* + 1, *z*]
O32–H32	1.965	152.26	2.718	O39W [−*x* + 1, *y* + 1/2, −*z* + 1]
Between β-CD and guest molecules				
N1–H1A	2.178	147.25	2.965	O8 [*x*, *y*, *z* + 1]

cule. However, the amino of *p*-aminobenzoic acid forms hydrogen bond, which is listed in Table 2, with the adjacent β-CD 3-OH groups. Therefore, the guest is held in the cavity mainly by van der Waals contacts and hydrogen bonds.

In the β-CD–*o*-aminobenzoic acid complex, there are three guest molecules (a, b, and c) per asymmetric unit (Fig. 2b). The distances between the centers of the two aromatic rings of a and c and the centers of the O-4 planes of the two β-CDs B and C are 0.969 and 1.422 Å, respectively. That is to say the two guest molecules (a and c) are only shallowly encapsulated in the two hydrophobic β-CD cavities, and the two guest molecules are incorporated into the β-CD cavities with the carboxyl and amino groups emerging from the primary faces of the β-CD dimer because of the steric hindrance of the two groups. Guests a and c make angles of 52.24° and 72.05° with O-4 planes of the two β-CD molecules B and C, respectively. The corresponding distances from center to center of the two aromatic rings and the angle between the two aromatic rings are 9.440 Å and 21.70°. The third guest molecules b, situated in two directions with occupancy factors of 0.72 and 0.28, are found in the middle of the dimer approximately perpendicular to its 7-fold axis. A similar motif has been described in the literature for the dimeric β-CD complex.[14] The angles between the aromatic rings of guest molecule b and guests a and c are 45.60° and 66.50°, respectively. There is no conventional hydrogen bond formed between guest a and c and the two host molecules. Obviously, van der Waals contacts are the main forces to keep the guests a and c in position. However, a number of hydrogen bonds that contribute to stabilize the dimeric β-CD complex formed among the guest, water

Table 3
Hydrogen bonds between the two β-CDs molecules B and C and of the two β-CDs with the guest molecule and water molecules

D–H	*d*(H···A) (Å)	∠DHA (°)	*d*(D···A) (Å)	*A*
Between β-CD molecules and water molecules				
O10–H10	1.900	167.29	2.725	O77W [*x*, *y*, *z*]
O12–H12	1.935	152.27	2.707	O92W [*x* + 1, *y*, *z* + 1]
O15–H15	1.878	158.35	2.677	O78W [*x* + 1, *y*, *z*]
O32–H32	1.825	171.14	2.657	O88W [*x*, *y*, *z* + 1]
O35–H35	1.881	168.24	2.709	O84W [*x*, *y*, *z*]
O40–H40A	1.920	167.61	2.746	O93W [*x* + 1, *y*, *z* + 1]
O42–H42	1.865	163.12	2.680	O99W [*x* + 1, *y*, *z* + 1]
O45–H45	1.874	174.77	2.711	O83W [*x* + 1, *y*, *z* + 1]
O65–H65	2.109	136.39	2.778	O103W [*x*, *y*, *z* + 1]
O65–H65	1.954	162.87	2.768	O85W [*x*, *y*, *z* + 1]
O68–H68	2.048	152.55	2.820	O97W [*x* + 1, *y* + 1, *z*]
O70–H70	2.293	107.71	2.671	O81W [*x* + 1, *y*, *z* + 1]
Between β-CD molecules and guest molecules				
O8–H8	2.473	126.44	3.047	O76 [*x*, *y*, *z*]
O76–H76A	2.233	163.20	3.047	O8 [*x*, *y*, *z*]
Between two β-CD molecules				
O8–H8	2.344	113.49	2.787	O48 [*x*, *y*, *z*]
O17–H17	2.152	173.12	2.988	O38 [*x*, *y*, *z*]
O18–H18	2.413	99.80	2.687	O38 [*x*, *y*, *z*]
O43–H43	2.017	161.63	2.827	O13 [*x*, *y*, *z*]
O48–H48	2.316	115.85	2.787	O8 [*x*, *y*, *z*]
O48–H48	2.411	121.26	2.937	O7 [*x*, *y*, *z*]
O57–H57	2.457	126.68	3.034	O33 [*x*, *y*, *z*]
O63–H63	2.183	127.94	2.779	O28 [*x*, *y*, *z*]

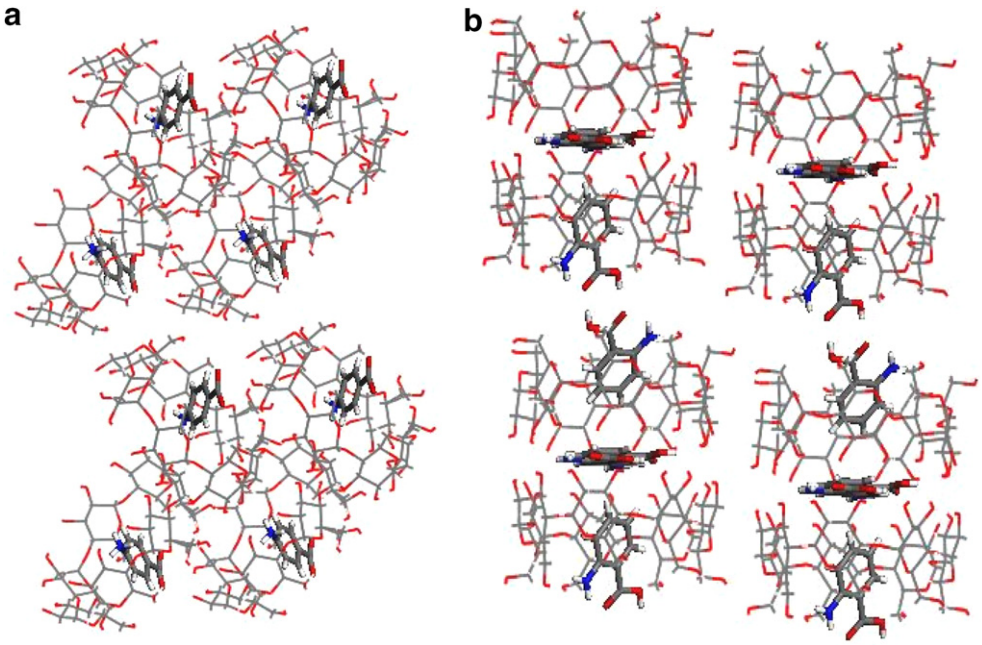

Figure 3. (a) Crystal packing of the complex β-CD–*p*-aminobenzoic acid. (b) Crystal packing of the complex β-CD–*o*-aminobenzoic acid. All water molecules are omitted.

molecules and O6 atoms of the two β-CDs are listed in Table 3. For example, a hydrogen bond forms between the guest molecule a and a water molecule ($d_{[H1A\cdots O86]}$ = 2.344 Å, $d_{[N1\cdots O86]}$ = 2.968 Å, ∠N1–H1A···O86=128.01°).

Crystal packing: Crystal structures of the β-CD inclusion complexes are classified into three types which are cage-type, channel-type, and layer-type according to the host–guest interactions.[15] Figure 3a shows that the β-CD–*p*-aminobenzoic acid complex packs in 'herring-bone' style, and both sides of each macrocycle cavity are blocked by glucose residues of neighboring molecules leading to a typical cage structure. Numerous hydrogen bonds of type O–H···O and N–H···O link neighboring cyclodextrin rings either directly or via bridges of water molecules.

In the β-CD–*o*-aminobenzoic acid complex, as shown in Figure 3b, the two β-CD molecules are arranged in a channel-packing mode approximately parallel to the crystal *c*-axis, frequently observed in the β-CD complexes.[15] Two β-CD monomers assemble through hydrogen bonds of type O–H···O listed in Table 4 to form the β-CD dimer. A summary of intermolecular hydrogen bonds that are crucial for packing is given in Table 4, excluding the hydrogen bonds in which water molecules are donors.

In summary, analysis of the structure of the β-CD–*p*-aminobenzoic acid and β-CD–*o*-aminobenzoic acid inclusion complexes shows that the guest molecule along with the co-crystallized water molecules plays an important role in the formation of the complex and the crystal packing. The *p*-aminobenzoic acid molecules are deeply included in the β-CD cavities, while the *o*-aminobenzoic acid molecules are less deeply included because of the severe steric hindrance of the latter. The structure of the β-CD-*o*-aminobenzoic acid complex revealed a 2:3 stoichiometry, with two *o*-aminobenzoic acid molecules included in the cavities of a β-CD dimer and a third *o*-aminobenzoic acid molecule at the interface between two layers of β-CD dimers. It is this third *o*-aminobenzoic acid molecule that provides the major source for the stabilization of the complex and the crystal packing.

Table 4
Intermolecular hydrogen bonds

D–H	*d*(H···A) (Å)	∠DHA (°)	*d*(D···A) (Å)	*A*
Between channels				
O5–H5	1.881	172.93	2.715	O70 [*x*, *y* + 1, *z*]
O20–H20	2.029	175.39	2.869	O35 [*x* + 1, *y* + 1, *z* + 1]
O27–H27	1.896	166.13	2.719	O47 [*x* + 1, *y* + 1, *z* + 1]
O30–H30	1.996	147.75	2.743	O10 [*x*, *y* + 1, *z* + 1]
O50–H50	2.067	172.43	2.901	O65 [*x*, *y*, *z* + 1]
O57–H57	2.283	118.26	2.781	O17 [*x*, *y* + 1, *z* + 1]
O60–H60	1.888	176.17	2.728	O40 [*x*, *y* + 1, *z* + 1]
Between guest molecules				
O74–H74A	1.708	175.75	2.546	O71 [*x* + 1, *y* + 1, *z* + 1]
O72–H72	1.866	163.44	2.681	O73 [*x* + 1, *y* + 1, *z* + 1]

1. Experimental

Crystallization: *p*-Aminobenzoic acid (obtained from Guangfu Fine Chemical Graduate School of Tianjin) and β-CD (purchased from the Kewei Company of Tianjin University) in a 1:1 molar ratio were fully dissolved separately in ethanol and water, and then the two solutions were mixed and stirred at 70 °C for two hours. The mixture was filtered at this temperature, stored at room temperature, and crystals were obtained after 7 days. Single crystals of the β-CD–*o*-aminobenzoic acid complex were obtained by a similar method.

X-ray diffraction experiments: A single crystal of each complex was mounted in a capillary tube in the presence of a small amount of mother liquor. X-ray diffraction experiments were carried out using a SMART CCD (Bruker) with Mo Kα radiation (λ = 0.71073 Å) operating at 50 kV, 30 mA. A total of 20415 (β-CD–*p*-aminobenzoic acid complex) and 22114 (β-CD–*o*-aminobenzoic acid complex) reflections were measured in the θ-range 2.05–27.83° (β-CD–*p*-aminobenzoic acid complex) and 1.29–25.00° (β-CD–*o*-aminobenzoic acid complex), respectively. Data reduction was carried out with the program SAINT, including semiempirical absorption correction with SADABS. Crystal data collection and refinement details are listed in Table 5.

Structure solution and refinement: The structures of the two complexes were determined by direct methods and refined using

Table 5
Crystallographic data

	β-CD–*p*-aminobenzoic acid	β-CD–*o*-aminobenzoic acid
Chemical formula	$C_{42}H_{70}O_{35}\cdot C_7H_7NO_2\cdot 5H_2O$	$2C_{42}H_{70}O_{35}\cdot 3C_7H_7NO_2\cdot 23H_2O$
Formula weight	1362.20	3095.74
Temperature (K)	294(2)	113(2)
Wavelength (Å)	0.71073	0.71070
Crystal system	Monoclinic	Triclinic
Space group	$P2_1$	$P1$
a (Å)	15.2196(10)	15.249(2)
b (Å)	10.2279(7)	15.2998(16)
c (Å)	20.9321(14)	17.853(3)
α (°)	90	99.5650(10)
β (°)	110.9270(10)	113.421(5)
θ (°)	90	101.931(2)
Volume (Å^3)	3043.4(4)	3593.7(9)
Z	2	1
Calculated density (mg/m^3)	1.486	1.430
Absorption coefficient (mm^{-1})	0.132	0.128
$F(000)$	1448	1650
Crystal size (mm)	$0.32 \times 0.28 \times 0.22$	$0.22 \times 0.20 \times 0.18$
Theta range for data collection (°)	2.05–27.83	1.29–25.00
Limiting indices	$-19 \leqslant h \leqslant 19$, $-13 \leqslant k \leqslant 13$, $-16 \leqslant l \leqslant 27$	$-10 \leqslant h \leqslant 18$, $-18 \leqslant k \leqslant 18$, $-21 \leqslant l \leqslant 20$
Reflections collected/unique	20415/14052	22114/12576
R (int)	0.0105	0.0391
Data/restraints/parameters	14052/33/828	12576/184/2008
Goodness-of-fit on F^2	1.050	1.027
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Final R indices [$F^2 > 2\sigma(F^2)$]	$R_1 = 0.0702$, $wR_2 = 0.2009$	$R_1 = 0.0715$, $wR_2 = 0.1876$
R indices (all data)	$R_1 = 0.0805$, $wR_2 = 0.2153$	$R_1 = 0.0803$, $wR_2 = 0.1994$
Max. and min. transmission	0.9716 and 0.9591	0.9773 and 0.9723
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Largest difference peak and hole (e/Å^3)	0.904 and −0.568	1.151 and −0.497

full-matrix least-squares based on F^2 with the program SHELX, based on 828 parameters and 33 restraints (β-CD–*p*-aminobenzoic acid complex) and 2008 parameters and 184 restraints (β-CD–*o*-aminobenzoic acid complex), respectively. The refinement converged at $R_1 = 0.0702$ and 0.0805 (β-CD–*p*-aminobenzoic acid complex) and $R_1 = 0.0715$ and 0.0803 (β-CD–o-aminobenzoic acid complex) for observed ($F^2 > 2\sigma(F^2)$) and all reflections, respectively. Water molecules were located on a difference Fourier map. All non-hydrogen atoms were refined anisotropically. Except for those hydrogen atoms attached to the water molecules, all the other hydrogen atoms were added in ideal positions and refined as riding models.

Supplementary data

Tables of atomic coordinates, bond lengths, and bond angles have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 689669 for the β-CD–*p*-aminobenzoic acid complex and 689670 for the β-CD–*o*-aminobenzoic acid complex. These data may be obtained free of charge, on request, from The Director, Cambridge Crystallographic Data Center, 12 Union Road, Cambridge, CB2lEZ, UK (fax: + 44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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