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A Novel Pseudo-Polyrotaxane Structure Composed of Cyclodextrins and a Straight-Chain Polymer: Crystal Structures of Inclusion Complexes of β-Cyclodextrin with Poly(trimethylene oxide) and Poly(propylene glycol)

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Cyclodextrins (CDs) are cyclic oligosaccharides with six (α-), seven (β-), or eight (γ-) α-1,4-linked glucose units which form inclusion complexes with various guest molecules.[1] CDs adopt a truncated conical structure, having the primary hydroxyl groups on the narrow (head or primary) side and the secondary hydroxyl groups on the wide (tail or secondary) side. Recently, CDs have been described as supramolecular assemblies serving as molecular devices, such as the molecular tube.[2−4] A molecular tube composed of CDs was synthesized by the formation of polyrotaxanes using poly(ethylene glycol) as a guest molecule.[3] A structural analysis of such polyrotaxanes is necessary to elucidate the interactions between hosts (CDs) and guests and/or between hosts and to obtain information about suitable combinations of guests and hosts. The crystal structures of inclusion complexes of α-CD with tetra(ethylene glycol) and hexa(ethylene glycol) have been determined,[5] and some inclusion complexes of β-CD with small straight-chain guests have been reported.[6−12] In these complexes, the guest molecules are strictly homogeneous having the same molecular weight (MW); the longest guest molecule among them is tridecanoic acid.[12] Here we report the crystal structures of inclusion complexes of β-CD with polymers, poly(trimethylene oxide) (P3MO, $(-CH_2CH_2CH_2O-)_n$, average MW = 1400, crystal structure **1**), and poly(propylene glycol) (PPG, $(-CH_2CH(CH_3)O-)_n$, average MW = 425, crystal structure **2**). P3MO and PPG with an all trans-conformation are approximately 97 and 22 Å long and may penetrate 14 and three β-CDs, respectively.

Crystallization and data collections at low temperature were carried out as described below.[13] The initial phase angles were determined by the isomorphous replacement method, using the coordinates of β-CD of the crystal structure of the β-CD/Z-9-dodecan-1-ol inclusion complex.[10] Guests and water molecules were located from $(F_o - F_c)$ an electron density map. In both crystal structures **1** and **2**, the $(F_o - F_c)$ electron density with a rod shape indicated a straight chain structure of guests (the electron density for P3MO is shown in Figure 1); however, only clear peaks on the primary narrow sides of β-CDs could be assigned as atoms of guests. Thus, the guest structures were built into the electron density map, assuming that guests have an all-trans conformation. All atoms of guests were refined as carbon atoms, and the methyl groups of PPG could not be located in the electron density map maybe due to the strong disordered structure. Atoms of β-CD were refined anisotropically, and atoms of guests and solvent molecules were refined isotropically. Hydrogen atoms except hydroxyl hydrogen atoms were introduced based on geometrical calculations and were not refined. By the full matrix least-squares method using program SHELX97,[14] both structures were refined to R-factors of 0.149 (crystal structure **1**) and 0.109 (crystal structure **2**).

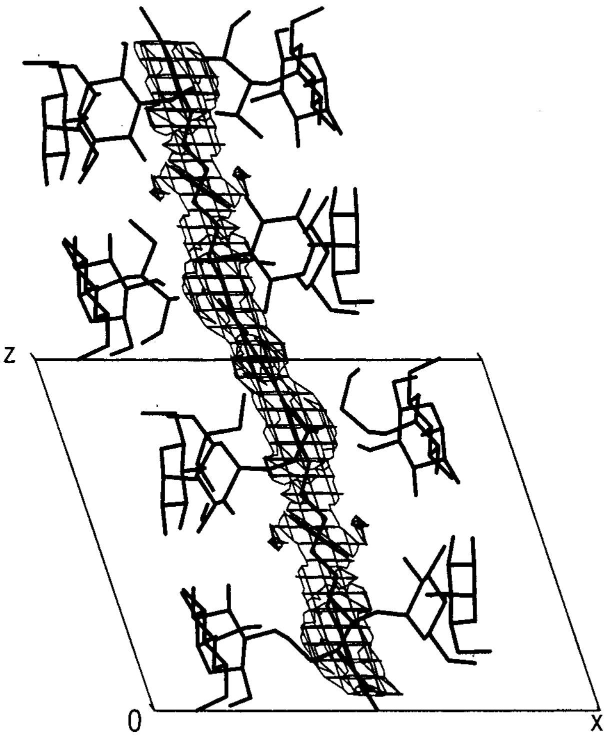

Figure 1. $(F_o - F_c)$ electron density map for P3MO (crystal structure **1**) contoured at 2.5σ with the final model.

In both of the refined crystal structures **1** and **2**, the structures of host β-CDs are very similar to each other, and the electron density of P3MO is more interpretable than that of PPG where the branched structure could not be seen. Therefore, the structural description concentrates on crystal structure **1**. β-CDs are arranged tail-to-tail to form a one-dimensional column structure as shown in Figure 2,[15] and the crystallographic 2-fold axes exist between the β-CDs. All of the secondary hydroxyl groups of β-CD molecules take part in intermolecular hydrogen bonding to an adjacent molecule, while there is only one intermolecular hydrogen bond between primary hydroxyl groups. β-CDs are not stacked in a straight line but form a slightly inclined column.

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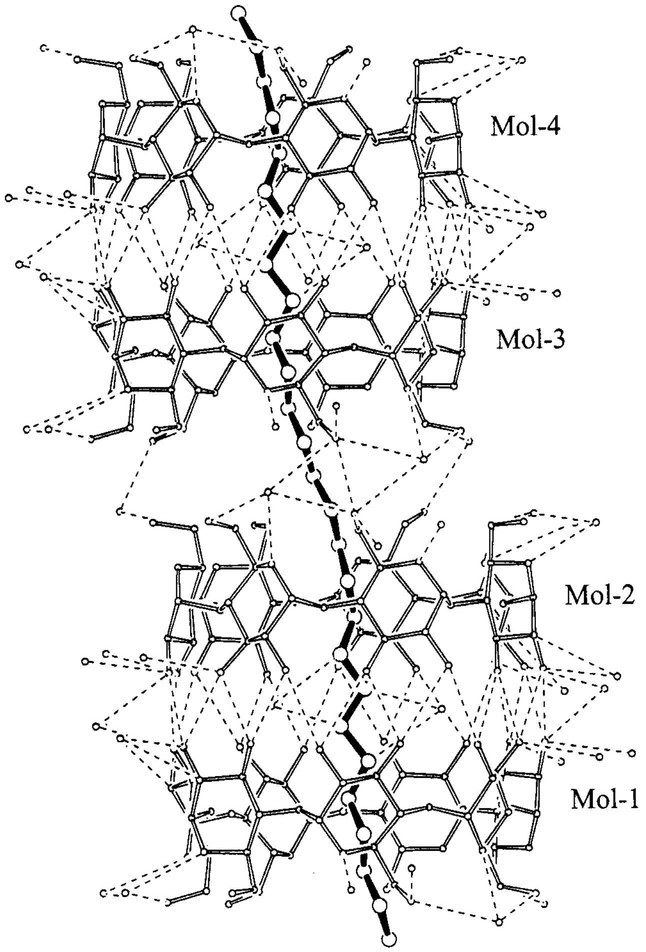

Figure 2. Column structure composed of four symmetry-related β-CDs (Mol-1, -2, -3, and -4) and P3MO, viewed from the *b*-axis (for clarity, molecules are rotated by 10° along the vertical axis). The β-CDs and P3MO are shown as open and solid bonds, respectively, and intermolecular hydrogen bonds as dotted lines. Solvent molecules which form direct hydrogen bonds with β-CDs are as open circles with hydrogen bonds. Crystallographic 2-fold axes are between Mol-1 and Mol-2, Mol-2 and Mol-3, and Mol-3 and Mol-4.

This is because β-CDs shift by about 2.5 Å between the primary sides. Such a column of β-CDs is found in the other β-CD inclusion complexes with a space group of *C*2, where two β-CDs contain a guest in the tail-to-tail orientation.

P3MO penetrates the center of the column of β-CDs. In the model presented, seven atoms are included in a β-CD. The atom between the primary sides of β-CDs is on the crystallographic 2-fold axis. As in the crystal structures of β-CD with *n*-octanol and pyrene,[11] 6.5 atoms of P3MO with one β-CD are located in the asymmetric unit. The all-*trans* conformation of P3MO is restrained through refinement using geometrical restraints;[14] the maximum deviation from the trans conformation is 33°. Almost all distances less than 4.8 Å between β-CD and P3MO are found on the primary side, because the cavity size of the primary side is inherently narrower than that of the secondary side and because the shift of a β-CD between the primary sides leads to almost the same internal diameter as in α-CD (4.5 Å), as shown in Figure 3. Therefore, the conformation of P3MO on the primary side is thought to be correct, giving the clear ($F_o - F_c$) electron density and many host–guest interactions. On the other hand, the electron density of P3MO around the secondary sides of β-CDs is very poor, indicating that P3MO is highly disordered on the secondary sides. Thus, the conformation of P3MO around the secondary side is still unclear.

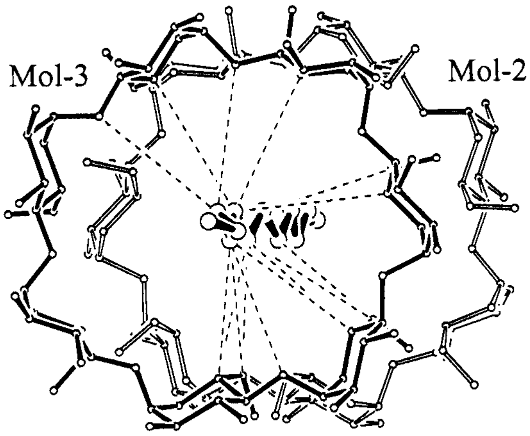

Figure 3. Structures of Mol-2 and Mol-3 with P3MO viewed down the plane of β-CD. Distances less than 4.8 Å between β-CD (Mol-3) and P3MO are shown as dotted lines.

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Supporting Information Available: Tables of crystal data, structure refinement data, atomic coordinates, bond lengths and angles, and displacement parameters for **1** and **2** and the ($F_o - F_c$) electron density map for PPG contoured at 2.5σ with the final model. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) P3MO and PPG were isolated and fractionated by Sephadex LH-20 column chromatography using methanol as solvent. Each of the molecular weights was estimated by a GPC method in THF as solvent. The molecular weight was calibrated by standard poly(styrenes). GPC determination was carried out with a Tosoh CCP&6010 system (column G3000HXL and G2000HXL). Crystals of the β-CD/P3MO and β-CD/PPG inclusion complexes were prepared by dissolving β-CD and guests in 1:1 (based on MW of a repeat unit) molar ratio in water at 70 °C. By slow cooling of the solutions to 25 °C, crystals with the size of 0.1 × 0.1 × 0.05 mm were obtained. Crystal structure **1**: diffractometer,

Rigaku R-Axis IV; radiation, Mo Kα; wavelength, 0.710 73 Å; maximum $2\theta = 50°$; temperature of measurement, 110 K; chemical formula, $C_{42}H_{70}O_{35}/1.625(C_3H_6O_1)/13H_2O$. Crystal data: space group = *C*2, $a = 19.369(4)$, $b = 24.540(3)$, $c = 15.983(6)$ Å, $\beta = 108.92(2)°$, $V = 7186(8)$ Å^3, $Z = 4$, *R*-factor ($I_o > \sigma(I_o)$, 3199 reflections) = 0.149, *R*-factor ($I_o > 2.0\sigma(I_o)$, 2314 reflections) = 0.135. Crystal structure **2**: diffractometer, Rigaku R-Axis IV; radiation, Mo Kα; wavelength, 0.710 73 Å; maximum $2\theta = 45°$; temperature of measurement, 110 K; chemical formula, $C_{42}H_{70}O_{35}/1.625(C_3H_6O_1)/13H_2O$. Crystal data: space group = *C*2, $a = 19.332(8)$, $b = 24.572(6)$, $c = 15.961(9)$ Å, $\beta = 109.00(5)°$, $V = 7521(9)$ Å^3, $Z = 4$, *R*-factor ($I_o > \sigma(I_o)$, 2655 reflections) = 0.109, *R*-factor ($I_o > 2.0\sigma(I_o)$, 1902 reflections) = 0.100. Atomic coordinates of these structures have been deposited with the Cambridge Crystallographic Data Centre.

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