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Structures of polyrotaxane models

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Abstract

Structures of complexes of hexa(ethylene glycol) with cyclomaltohexaose (α-CD) and that of tetra(ethylene glycol) dibromide with α-CD have been determined by X-ray diffraction studies. α-CDs form columns in a head-to-head (the side of secondary hydroxyl groups) and tail-to-tail (the side of primary hydroxyl groups) fashion. Ethylene glycol chains are included in channels formed by α-CDs. © 1998 Elsevier Science Ltd

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1. Introduction

Recently, rotaxanes and catenanes have attracted renewed attention because of their unique structures and properties [1]. Polyrotaxanes in which many ring molecules are threaded onto a polymer chain adopt a more sophisticated molecular architecture [2]. Previously, we reported the formation of inclusion complexes of cyclodextrins (CDs) with various polymers [3] and the preparation of polyrotaxanes in which many CDs are threaded onto a poly(ethylene glycol) (PEG) chain [4]. PEGs having large substituents at both ends and large cyclic oligo(ethylene glycol)s (crown ethers) did not form complexes with cyclomaltohexaose (α-CD) [5]. The solid-state ^{13}C NMR spectra and X-ray diffraction studies (powder) of the complex with α-CD suggest that the complexes are 'channel type': a linear guest molecule is included in a tunnel formed by α-CDs [6]. Now we report on X-ray structural studies of the model complexes, a complex of hexa(ethylene glycol) with α-CD and that of tetra(ethylene glycol) dibromide with α-CD. The α-CDs form channel-type structures with inclusion of ethylene glycol chains.

2. Experimental

Complexes of α-CD with hexa(ethylene glycol) or tetra(ethylene glycol) dibromide were produced by adding hexa(ethylene glycol) or tetra(ethylene glycol) dibromide to saturated aqueous solutions of α-CD. The complexes were dissolved in water by heating. The clear aqueous solutions were allowed to stand in an evacuated jar for a week, affording single crystals of complexes suitable for X-ray studies.

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3. Results and discussion

The results of the X-ray studies are as follows: The crystal system of the complex between α-CD and hexa(ethylene glycol) is monoclinic, space group $C2$, with $a = 36.891$ Å, $b = 23.884$ Å, $c = 23.341$ Å, $\beta = 123.084°$. The composition of the complex is 3:1 [3 α-CDs:hexa(ethylene glycol)]. R-values are 11.4% (with 3 CDs and 25 water) and 9.8% [(with 3 CDs, 25 water, and hexa(ethylene glycol)]. Three CD molecules are contained in the asymmetric unit of the crystal. The structure could not to be solved by the direct methods but could be solved by the molecular replacement method [7]. The composition of the complex is 2:1 [2 α-CDs:tetra(ethylene glycol) dibromide]. The space group of the crystal of the complex between α-CD and tetra(ethylene glycol) dibromide is $C2$, with $a = 13.65$ Å, $b = 24.16$ Å, $c = 31.54$ Å, $\beta = 91.86°$. The coordinates obtained were refined using the program package SHELX (2) [8].

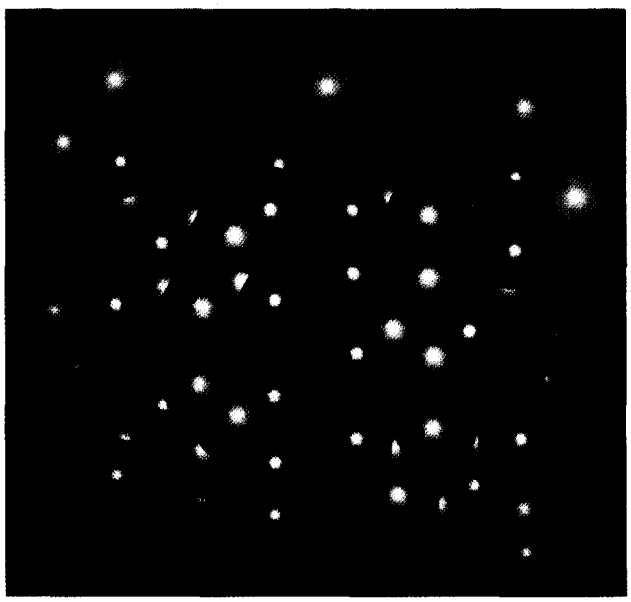

Fig. 1. Structure of the complex of α-CD with tetra(ethylene glycol) dibromide. Light blue shows water oxygen.

Fig. 1 shows the result of the X-ray study on the complex of α-CD with tetra(ethylene glycol) dibromide. Two α-CDs bind a single guest molecule to form a 2:1 complex in a face-to-face (secondary hydroxyl sides) fashion. All of the primary hydroxyl groups of the CDs are directed away from the cavity, indicating that there are no direct hydrogen bonds between α-CD and the guest molecule. Fig. 2a shows the structure of the complex formed between α-CD and hexa(ethylene glycol). CDs form infinite columns and are arranged in head-to-head (side of secondary hydroxyl groups) and tail-to-tail (side of primary

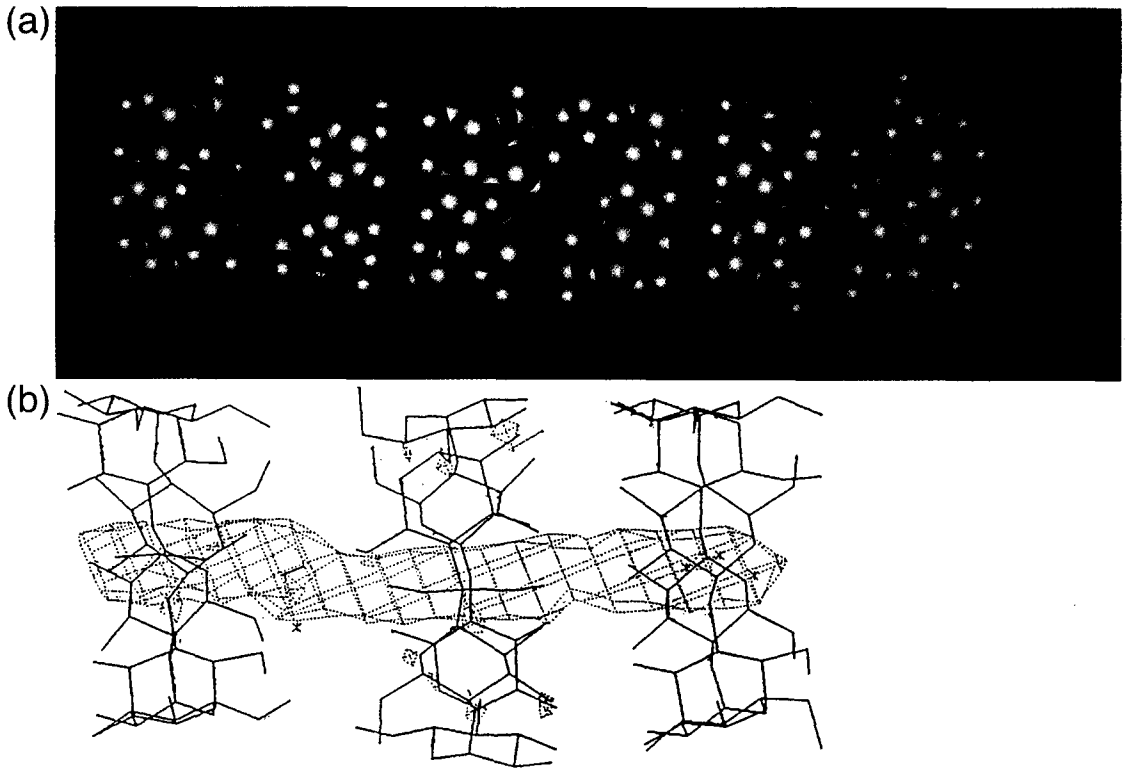

Fig. 2. (a) Structure of the complex of α-CD with hexa(ethylene glycol). (b) The electron density of hexa(ethylene glycol) in the complex with α-CD.

hydroxyl groups) fashion. Secondary hydroxyl groups are directly hydrogen-bonded to each other to form a tight hydrogen-bond network. Primary hydroxyl groups of neighbouring CDs are hydrogen-bonded by way of single water molecules. The formation of a tight hydrogen-bonding network seems to stabilize the formation of the polyrotaxane structure. A hexa(ethylene glycol) chain is included in the channel formed by α-CDs. Although carbon and oxygen atoms of the guest are indistinguishable so that precise positions of C(O) atoms could not be determined, clear electron densities in the channel show the presence and location of the guest.

Although the conformation of the hexa(ethylene glycol) chain has not been determined, the electron density residual clearly located at the center of the CD molecules corresponds to the zigzag chain of hexaethylene glycol. The length of the density is consistent with the length of the molecule assuming a planar zigzag chain. A zigzag conformation is one of the favored conformations of the PEG chain as shown by X-ray studies and conformational energy calculations [9]. Fig. 2b shows the electron density of hexa(ethylene glycol) in the complex.

CDs form a honeycomb structure, as shown in Fig. 3 in which neighbouring columns contact each other. The side view of the stacked columns showed that they form a layer structure: a hydrophillic layer consisting of secondary hydroxyl groups and primary hydroxyl groups and a hydrophobic layer consisting of the carbon–hydrogen aspect of the glucose residues.

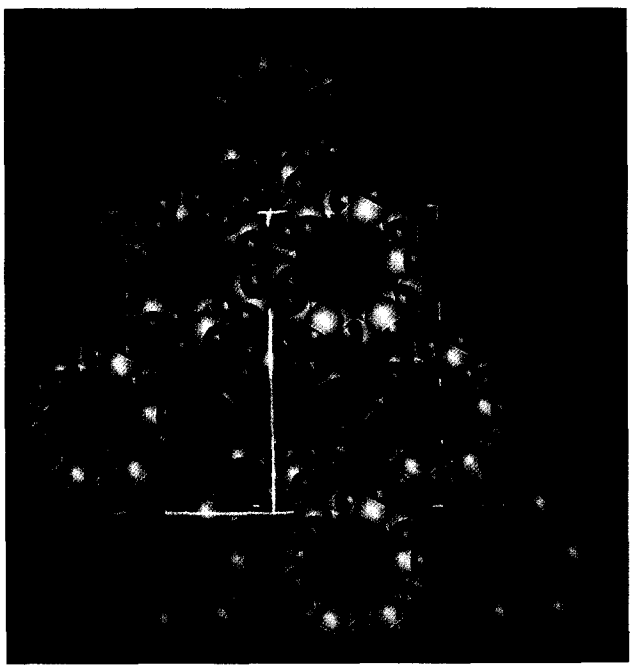

Fig. 3. Crystal packing of the complexes of α-CD with hexa(ethylene glycol).

Polyrotaxanes, in which many CDs are threaded onto a polymer chain, may be expected to adopt a structure similar to that of the model complexes.

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