The Structure of the Cyclodextrin Complex. VIII. Crystal Structures of α-Cyclodextrin Complexes with 2-Pyrrolidone and *N,N*-Dimethylformamide

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Crystal structures of α-cyclodextrin complexes with *N,N*-dimethylformamide and 2-pyrrolidone were determined by the X-ray method. The pentahydrated crystals of both complexes are orthorhombic, and the space group is $P2_12_12_1$ with $Z=4$. The cell dimensions are $a=13.750(1)$, $b=15.318(1)$, and $c=24.544(2)$ Å for the *N,N*-dimethylformamide complex, and $a=13.852(1)$, $b=15.373(1)$, and $c=24.353(2)$ Å for the 2-pyrrolidone complex. The structures were determined by assuming the same α-cyclodextrin packing in the crystal as that found in the isomorphous *p*-nitrophenol complex, and refined by the block-diagonal least-squares method to the final *R*-values of 0.054 for the *N,N*-dimethylformamide complex (5151 reflections) and 0.051 for the 2-pyrrolidone complex (5165 reflections). In both complexes, the guest molecules are included in the α-cyclodextrin cavity. The *N,N*-dimethylformamide molecule is in van der Waals contact with the host α-cyclodextrin molecule, while the 2-pyrrolidone molecule forms a weak N–H···O hydrogen bond with a glycosidic oxygen atom of α-cyclodextrin. The carbonyl oxygen atom of *N,N*-dimethylformamide and 2-pyrrolidone is hydrogen-bonded to water molecules of hydration located at the primary hydroxyl side of α-cyclodextrin. The tilt-angle of the glucose residue against the plane through six glycosidic oxygen atoms indicates clearly that the macro-cyclic conformation of α-cyclodextrin is affected by the packing as well as the size and shape of the guest molecule. The α-cyclodextrin molecules in the crystal are arranged parallel to the ac plane to form molecular layers. Three water molecules are located near the guest molecule, while the other two water molecules fill the intermolecular space.

Crystal structures of several α-cyclodextrin (α-CDx) complexes with benzene derivatives have already been determined by the X-ray method,[1-6] and it has been shown that the benzene ring can be included in the α-CDx cavity. On the other hand, the circular dichroism studies have shown that cyclodextrins form complexes with non-aromatic ring compounds, such as substituted cyclohexanones.[7] In this paper, we deal with the crystal structure of the α-CDx–2-pyrrolidone (1:1) complex to investigate the geometry of inclusion of a non-aromatic compound.

α-CDx dissolves in organic solvents such as DMSO and *N,N*-dimethylformamide (DMF). The X-ray study of α-CDx crystals obtained from a DMSO–methanol solution has shown that the α-CDx molecule includes DMSO and methanol molecules simultaneously.[8] The crystal structure of α-CDx crystallized from DMF–water solution was also determined to investigate the α-CDx–DMF interaction.

Experimental

Crystals of the α-CDx complex with 2-pyrrolidone (PRD) were obtained by cooling an aqueous solution containing α-CDx and PRD in 1:1 molar ratio. The α-CDx–DMF (1:1) complex was crystallized from a DMF–water (1:1) solution. Lattice parameters and reflection intensities were measured on a Rigaku automatic four-circle diffractometer with graphite-monochromatized Cu $K\alpha$ radiation. Intensity data were collected up to 150° in 2θ by using the θ-2θ scan technique. For the DMF complex, 5465 independent reflections were obtained, but 314 reflections with $|F_o| < 3\sigma(F)$ were treated as unobserved. The same treatment was done for 245 reflections of the 5410 observed ones for the PRD complex. No corrections were made for absorption and extinction.

Crystal Data: α-CDx–MDF pentahydrate, $C_{36}H_{60}O_{30}\cdot C_3H_7ON\cdot 5H_2O$: *F.W.*=1136.0, orthorhombic, space group $P2_12_12_1$, $Z=4$, $a=13.750(1)$, $b=15.318(1)$, $c=24.544(2)$ Å, $V=5169.5(2)$ Å^3, $D_x=1.460$, $D_m=1.454$ g·cm^{-3}.

α-CDx–PRD pentahydrate, $C_{36}H_{60}O_{30}\cdot C_4H_7ON\cdot 5H_2O$: *F.W.*=1148.0, orthorhombic, space group $P2_12_12_1$, $Z=4$, $a=13.852(1)$, $b=15.373(1)$, $c=24.353(2)$ Å, $V=5186.2$ Å^3, $D_x=1.470$, $D_m=1.461$ g·cm^{-3}.

Determination and Refinement of the Structure

Crystals of the α-CDx complexes with DMF and PRD are isomorphous with the crystals of di-substituted benzene complexes.[1,2,5] A set of coordinates of α-CDx found in the *p*-nitrophenol complex[5] was used to determine initial phases for these complexes. The guest and water molecules were found on Fourier and difference-Fourier maps. Seventy hydrogen atoms in the DMF complex and sixtyfive ones in the PRD complex were found on the difference-Fourier maps. A primary hydroxyl group (O(6,G4)) and two water molecules (W4 and W5) were revealed to be statistically disordered in both complexes. Their occupancies were estimated from an electrondensity map, but they were not refined. The refinement of atomic parameters was carried out by the block-diagonal least-squares method, the quantity minimized being $\Sigma w(|F_o|-|F_c|)^2$, with $w=1.0$ for all the reflections used. Temperature factors of hydrogen atoms were not refined, but fixed as equal to the isotropic ones of heavier atoms to which the hydrogen atoms are bonded. The final *R*-values were 0.054 and 0.051 for the DMF and PRD complexes, respectively. The atomic parameters are listed in Tables 1 and 2.*

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* The tables of observed and calculated structure factors of both complexes and those of bond distances, bond angles, and conformation angles are kept at the Office of the Chemical Society of Japan (Document No. 7927).

TABLE 1. FINAL ATOMIC PARAMETERS ($\times 10^4$) FOR THE NON-HYDROGEN ATOMS

The anisotropic temperature factors are of the form: $\exp[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{23}kl+B_{31}lh)]$. OC indicates the occupancy factor for the disordered atom.

α-Cyclodextrin-N,N-dimethylformamide complex

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{23}	B_{31}	OC
C(1,G1)	1565(4)	-501(3)	6915(2)	38(3)	31(2)	10(1)	0(4)	4(2)	0(2)	
C(2,G1)	1278(4)	-1243(3)	6531(2)	47(3)	32(2)	9(1)	-20(4)	5(2)	1(2)	
C(3,G1)	1855(4)	-1165(3)	6007(2)	45(3)	21(2)	10(1)	-2(4)	1(2)	-2(3)	
C(4,G1)	1738(3)	-264(3)	5764(2)	39(3)	25(2)	9(1)	-2(4)	1(2)	5(2)	
C(5,G1)	2018(4)	440(3)	6179(2)	59(3)	22(2)	9(1)	3(4)	-1(2)	2(3)	
C(6,G1)	1844(5)	1362(3)	5971(2)	99(5)	25(2)	15(1)	12(6)	3(3)	-3(4)	
O(2,G1)	1489(3)	-2053(2)	6802(1)	85(3)	30(2)	12(1)	-46(4)	10(2)	-13(2)	
O(3,G1)	1498(3)	-1813(2)	5632(1)	67(3)	21(1)	10(1)	-16(3)	-2(2)	-4(2)	
O(4,G1)	2409(2)	-228(2)	5314(1)	31(2)	32(1)	8(1)	4(3)	7(1)	2(2)	
O(5,G1)	1428(3)	319(2)	6659(1)	54(2)	27(1)	10(1)	25(3)	1(2)	1(2)	
O(6,G1)	871(4)	1487(3)	5785(2)	101(4)	46(2)	18(1)	53(5)	13(2)	0(3)	
C(1,G2)	2072(3)	41(3)	4795(2)	31(2)	31(2)	10(1)	2(4)	8(2)	0(2)	
C(2,G2)	2299(3)	-684(3)	4389(2)	37(3)	25(2)	11(1)	-3(4)	4(2)	-1(2)	
C(3,G2)	3381(3)	-834(3)	4369(2)	36(2)	23(2)	10(1)	-2(4)	2(2)	5(2)	
C(4,G2)	3869(3)	19(3)	4251(2)	28(2)	21(2)	10(1)	6(3)	2(2)	0(2)	
C(5,G2)	3586(3)	750(3)	4634(2)	30(2)	21(2)	13(1)	5(4)	-2(2)	5(2)	
C(6,G2)	3983(4)	1632(3)	4466(3)	48(3)	23(2)	23(1)	-5(4)	-2(3)	9(3)	
O(2,G2)	1833(3)	-1483(2)	4552(1)	43(2)	34(2)	12(1)	-27(3)	4(2)	-2(2)	
O(3,G2)	3643(3)	-1437(2)	3944(1)	55(2)	20(1)	14(1)	1(3)	-7(2)	10(2)	
O(4,G2)	4911(2)	-153(2)	4334(1)	27(2)	26(1)	9(1)	9(3)	7(1)	3(2)	
O(5,G2)	2539(2)	820(2)	4635(1)	32(2)	22(1)	12(1)	11(3)	8(1)	7(2)	
O(6,G2)	3831(3)	1785(3)	3897(2)	64(3)	37(2)	27(1)	18(4)	33(2)	20(3)	
C(1,G3)	5587(3)	72(3)	3921(2)	33(2)	27(2)	7(1)	0(4)	3(2)	4(2)	
C(2,G3)	6216(3)	-727(3)	3826(2)	35(2)	25(2)	8(1)	0(4)	1(2)	-1(2)	
C(3,G3)	6720(3)	-971(3)	4352(2)	29(2)	19(2)	10(1)	6(3)	1(2)	2(2)	
C(4,G3)	7269(3)	-195(3)	4587(2)	33(2)	23(2)	7(1)	3(3)	2(2)	-1(2)	
C(5,G3)	6655(3)	644(3)	4600(2)	40(3)	20(2)	9(1)	1(4)	3(2)	-1(2)	
C(6,G3)	7256(4)	1460(3)	4707(2)	53(3)	21(2)	16(1)	-11(4)	1(2)	-4(3)	
O(2,G3)	5634(2)	-1442(2)	3627(1)	34(2)	27(1)	9(1)	4(3)	-11(2)	-3(2)	
O(3,G3)	7411(2)	-1654(2)	4269(1)	37(2)	21(1)	16(1)	17(3)	-3(2)	-2(2)	
O(4,G3)	7519(2)	-438(2)	5133(1)	30(2)	27(1)	7(1)	-3(3)	3(1)	-2(2)	
O(5,G3)	6182(2)	776(2)	4082(1)	33(2)	22(1)	9(1)	-1(3)	7(1)	-1(2)	
O(6,G3)	8122(3)	1498(3)	4389(2)	48(2)	40(2)	20(1)	-32(4)	12(2)	2(2)	
C(1,G4)	8474(3)	-254(3)	5318(2)	32(2)	25(2)	9(1)	-3(4)	-6(2)	3(2)	
C(2,G4)	8824(4)	-1061(3)	5619(2)	40(3)	27(2)	9(1)	10(4)	-6(2)	-2(2)	
C(3,G4)	8256(4)	-1196(3)	6146(2)	43(3)	17(2)	10(1)	6(4)	-3(2)	-3(2)	
C(4,G4)	8270(3)	-367(3)	6483(2)	38(3)	20(2)	8(1)	-1(4)	-2(2)	4(2)	
C(5,G4)	7876(4)	394(3)	6146(2)	45(3)	17(2)	9(1)	6(4)	-3(2)	3(2)	
C(6,G4)	7939(5)	1259(3)	6441(2)	77(4)	20(2)	12(1)	6(5)	-4(2)	0(3)	
O(2,G4)	8747(3)	-1810(2)	5271(1)	53(2)	33(2)	11(1)	28(3)	-15(2)	-6(2)	
O(3,G4)	8705(3)	-1889(2)	6446(1)	79(3)	22(1)	10(1)	29(3)	6(2)	5(2)	
O(4,G4)	7634(2)	-534(2)	6940(1)	35(2)	28(1)	6(1)	-7(3)	-2(1)	-2(2)	
O(5,G4)	8486(2)	485(2)	5670(1)	42(2)	20(1)	9(1)	-16(3)	-1(1)	3(2)	
O(6A,G4)	9093(15)	1450(11)	6539(7)	79(4)	23(7)	12(3)	-39(17)	-13(8)	8(11)	0.2
O(6B,G4)	7475(4)	1917(3)	6099(2)	73(3)	22(2)	16(1)	26(4)	-2(2)	2(3)	0.8
C(1,G5)	7982(3)	-335(3)	7473(2)	36(3)	29(2)	9(1)	-4(4)	-5(2)	-5(2)	
C(2,G5)	7812(4)	-1125(3)	7833(2)	41(3)	26(2)	9(1)	5(4)	-3(2)	-3(2)	
C(3,G5)	6732(4)	-1319(3)	7892(2)	41(3)	23(2)	10(1)	-6(4)	2(2)	-1(2)	
C(4,G5)	6160(3)	-501(3)	8042(2)	27(2)	28(2)	13(1)	-7(4)	-5(2)	-1(2)	
C(5,G5)	6433(3)	296(3)	7698(2)	34(3)	27(2)	11(1)	-1(4)	0(2)	-2(2)	
C(6,G5)	6029(4)	1152(3)	7901(2)	49(3)	27(2)	18(1)	9(5)	-3(3)	4(3)	
O(2,G5)	8310(3)	-1855(2)	7601(1)	58(2)	31(2)	13(1)	26(3)	2(2)	1(2)	
O(3,G5)	6633(3)	-1972(2)	8306(2)	67(3)	32(2)	17(1)	2(4)	16(2)	14(3)	
O(4,G5)	5156(2)	-705(2)	7943(1)	27(2)	39(2)	13(1)	-10(3)	-15(2)	0(2)	
O(5,G5)	7481(2)	396(2)	7692(1)	34(2)	24(1)	10(1)	-5(3)	-7(1)	0(2)	
O(6,G5)	6180(3)	1266(3)	8480(2)	50(2)	50(2)	18(1)	-4(4)	-29(2)	2(2)	
C(1,G6)	4448(4)	-527(3)	8339(2)	34(3)	33(2)	11(1)	2(4)	5(2)	2(3)	
C(2,G6)	3725(4)	-1266(4)	8365(2)	42(3)	38(2)	21(1)	-8(5)	28(3)	-17(3)	
C(3,G6)	3293(4)	-1397(3)	7791(2)	39(3)	24(2)	18(1)	-8(4)	13(2)	-2(3)	
C(4,G6)	2809(4)	-556(3)	7628(2)	40(3)	26(2)	7(1)	-3(4)	3(2)	-1(2)	
C(5,G6)	3461(4)	242(3)	7687(2)	49(3)	27(2)	9(1)	-8(4)	0(2)	-7(3)	
C(6,G6)	2891(5)	1095(3)	7644(2)	68(4)	29(2)	17(1)	3(5)	4(3)	-16(3)	
O(2,G6)	4159(4)	-2040(3)	8573(2)	78(3)	44(2)	41(1)	-14(4)	38(3)	-54(4)	
O(3,G6)	2590(3)	-2086(2)	7809(2)	54(3)	29(2)	25(1)	-35(4)	21(2)	-20(3)	
O(4,G6)	2544(2)	-630(2)	7066(1)	36(2)	30(1)	8(1)	5(3)	-1(1)	1(2)	
O(5,G6)	3926(3)	248(2)	8222(1)	47(2)	32(2)	8(1)	11(3)	-4(2)	-8(2)	
O(6,G6)	1983(3)	1078(3)	7924(2)	75(3)	55(2)	17(1)	51(5)	-7(2)	8(3)	
C(1,DF)	5343(10)	-1878(9)	6526(4)	233(15)	155(10)	22(2)	-139(21)	51(7)	-41(9)	
C(2,DF)	5072(11)	-1420(9)	5587(3)	292(17)	156(10)	13(1)	105(24)	-9(6)	4(9)	
C(3,DF)	4976(10)	-358(12)	6385(7)	123(11)	231(17)	83(6)	-81(26)	4(18)	11(14)	
N(DF)	5096(5)	-1157(4)	6131(2)	88(4)	59(3)	23(1)	-33(7)	-20(3)	12(4)	
O(DF)	4855(7)	212(6)	6121(5)	162(8)	104(6)	128(5)	-30(13)	-1(10)	-1(12)	
O(W1)	5055(3)	1203(3)	9388(2)	53(3)	89(3)	16(1)	-8(5)	1(3)	-6(3)	
O(W2)	42(4)	1059(4)	7520(2)	87(3)	83(3)	19(1)	-37(6)	-18(3)	28(3)	
O(W3)	106(4)	1565(4)	4664(2)	78(4)	92(4)	24(1)	24(6)	-1(3)	-3(3)	
O(W4A)	247(4)	2387(4)	6734(2)	62(4)	58(3)	23(1)	6(6)	4(3)	-20(4)	0.8
O(W4B)	-165(14)	3321(17)	7104(8)	34(11)	91(16)	17(4)	-49(23)	14(13)	5(11)	0.2
O(W5A)	-341(6)	3236(5)	3151(3)	84(5)	58(4)	29(2)	-11(8)	33(4)	-9(5)	0.7
O(W5B)	661(15)	3137(14)	4247(8)	105(16)	99(13)	34(5)	-37(25)	4(14)	-37(15)	0.3

TABLE 1. (Continued)

α-Cyclodextrin-2-pyrrolidone complex

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{23}	B_{31}	OC
C(1,G1)	1549(3)	-499(3)	6896(2)	39(2)	32(2)	10(1)	-1(4)	4(2)	5(2)	
C(2,G1)	1255(4)	-1222(3)	6507(2)	44(3)	37(2)	9(1)	-20(4)	5(2)	-5(2)	
C(3,G1)	1836(3)	-1154(3)	5979(2)	42(3)	22(2)	11(1)	-7(4)	2(2)	-4(2)	
C(4,G1)	1725(3)	-250(3)	5733(2)	35(2)	27(2)	9(1)	-5(4)	3(2)	5(2)	
C(5,G1)	1981(4)	449(3)	6156(2)	57(3)	22(2)	12(1)	7(4)	3(2)	4(3)	
C(6,G1)	1818(5)	1367(3)	5951(2)	106(5)	26(2)	15(1)	20(6)	2(2)	-4(4)	
O(2,G1)	1454(3)	-2031(2)	6780(1)	82(3)	28(2)	12(1)	-45(4)	10(2)	-15(2)	
O(3,G1)	1484(3)	-1801(2)	5604(1)	60(2)	22(1)	11(1)	-15(3)	0(1)	-5(2)	
O(4,G1)	2405(2)	-209(2)	5289(1)	27(1)	31(1)	8(1)	4(3)	5(1)	1(1)	
O(5,G1)	1402(3)	320(2)	6639(2)	57(2)	29(2)	11(1)	28(3)	1(2)	6(2)	
O(6,G1)	837(4)	1481(3)	5767(2)	114(4)	52(2)	19(1)	81(5)	18(2)	17(3)	
C(1,G2)	2076(3)	47(3)	4764(2)	29(2)	29(2)	10(1)	1(4)	8(2)	1(2)	
C(2,G2)	2309(3)	-681(3)	4360(2)	33(2)	27(2)	10(1)	-6(4)	3(2)	1(2)	
C(3,G2)	3391(3)	-832(3)	4353(2)	32(2)	25(2)	11(1)	-1(4)	-1(2)	1(2)	
C(4,G2)	3901(3)	16(3)	4228(2)	26(2)	20(2)	11(1)	6(3)	2(2)	1(2)	
C(5,G2)	3578(3)	759(3)	4598(2)	28(2)	22(2)	14(1)	4(3)	-1(2)	2(2)	
C(6,G2)	3973(4)	1636(3)	4409(2)	47(3)	20(2)	25(1)	-5(4)	3(3)	11(3)	
O(2,G2)	1843(2)	-1473(2)	4518(1)	39(2)	32(2)	12(1)	-24(3)	4(2)	-3(2)	
O(3,G2)	3659(2)	-1453(2)	3939(1)	47(2)	21(1)	14(1)	2(3)	-7(2)	6(2)	
O(4,G2)	4909(2)	-142(2)	4317(1)	26(1)	23(1)	9(1)	8(2)	5(1)	3(1)	
O(5,G2)	2545(2)	828(2)	4597(1)	29(2)	23(1)	13(1)	11(3)	6(1)	6(2)	
O(6,G2)	3816(3)	1754(3)	3833(2)	62(3)	36(2)	29(1)	14(4)	35(2)	20(3)	
C(1,G3)	5580(3)	57(3)	3894(2)	32(2)	26(2)	8(1)	0(4)	4(2)	4(2)	
C(2,G3)	6193(3)	-748(3)	3810(2)	31(2)	24(2)	8(1)	-1(4)	-2(2)	2(2)	
C(3,G3)	6708(3)	-970(3)	4347(2)	28(2)	19(2)	11(1)	2(3)	-1(2)	1(2)	
C(4,G3)	7267(3)	-187(3)	4559(2)	30(2)	22(2)	8(1)	-3(3)	1(2)	-1(2)	
C(5,G3)	6658(3)	650(3)	4565(2)	40(2)	20(2)	10(1)	-4(4)	4(2)	-5(2)	
C(6,G3)	7269(4)	1463(3)	4660(2)	56(3)	20(2)	16(1)	-19(4)	3(2)	-3(3)	
O(2,G3)	5608(2)	-1460(2)	3621(2)	33(2)	27(1)	9(1)	3(3)	-8(1)	-3(2)	
O(3,G3)	7386(2)	-1657(2)	4265(1)	35(2)	20(1)	16(1)	13(3)	-1(1)	-5(2)	
O(4,G3)	7530(2)	-406(2)	5109(1)	28(1)	27(1)	8(1)	-4(3)	4(1)	-2(1)	
O(5,G3)	6175(2)	765(2)	4043(1)	34(2)	20(1)	11(1)	-3(3)	8(1)	-3(2)	
O(6,G3)	8118(3)	1483(2)	4328(2)	51(2)	41(2)	22(1)	-36(4)	13(2)	2(2)	
C(1,G4)	8483(3)	-218(3)	5288(2)	30(2)	28(2)	10(1)	-5(4)	-3(2)	0(2)	
C(2,G4)	8847(3)	-1023(3)	5580(2)	33(2)	25(2)	10(1)	8(4)	-6(2)	-1(2)	
C(3,G4)	8290(3)	-1175(3)	6107(2)	38(2)	18(2)	10(1)	2(4)	-1(2)	-5(2)	
C(4,G4)	8293(3)	-359(3)	6454(2)	34(2)	21(2)	10(1)	-4(4)	-2(2)	2(2)	
C(5,G4)	7896(3)	408(3)	6123(2)	47(3)	17(2)	10(1)	6(4)	-4(2)	1(2)	
C(6,G4)	7967(5)	1273(3)	6428(2)	82(4)	18(2)	15(1)	2(5)	-6(2)	2(3)	
O(2,G4)	8789(2)	-1765(2)	5224(1)	42(2)	34(2)	12(1)	24(3)	-15(2)	-8(2)	
O(3,G4)	8732(3)	-1860(2)	6416(1)	71(2)	20(1)	11(1)	24(3)	-1(1)	-2(2)	
O(4,G4)	7657(2)	-532(2)	6912(1)	33(2)	26(1)	8(1)	-12(3)	-1(1)	0(1)	
O(5,G4)	8500(2)	511(2)	5642(1)	43(2)	22(1)	10(1)	-16(3)	-1(1)	-2(2)	
O(6A,G4)	9103(11)	1465(8)	6530(5)	95(11)	27(5)	21(3)	-37(10)	-18(7)	8(9)	0.3
O(6B,G4)	7485(4)	1934(3)	6098(2)	75(4)	16(2)	16(1)	5(4)	2(2)	-5(3)	0.7
C(1,G5)	7975(3)	-345(3)	7449(2)	34(2)	24(2)	10(1)	-4(4)	-4(2)	-6(2)	
C(2,G5)	7788(3)	-1150(2)	7801(2)	41(3)	27(2)	9(1)	11(4)	-2(2)	-3(2)	
C(3,G5)	6707(4)	-1331(3)	7840(2)	43(3)	25(2)	11(1)	-2(4)	1(2)	2(2)	
C(4,G5)	6154(3)	-509(2)	7994(2)	28(2)	24(2)	13(1)	-6(4)	-6(2)	-3(2)	
C(5,G5)	6450(3)	284(3)	7658(2)	34(2)	29(2)	11(1)	-2(4)	-4(2)	3(2)	
C(6,G5)	6044(4)	1141(3)	7873(2)	44(3)	26(2)	22(1)	9(4)	-1(3)	7(3)	
O(2,G5)	8300(3)	-1883(2)	7586(1)	56(2)	30(2)	13(1)	29(3)	1(2)	4(2)	
O(3,G5)	6546(3)	-2001(2)	8233(2)	82(3)	28(2)	18(1)	0(4)	10(2)	23(3)	
O(4,G5)	5155(2)	-697(2)	7884(1)	28(2)	37(2)	12(1)	-12(3)	-12(2)	1(2)	
O(5,G5)	7484(2)	375(2)	7670(1)	32(2)	22(1)	11(1)	-10(3)	-7(1)	1(2)	
O(6,G5)	6190(3)	1250(3)	8445(2)	47(2)	49(2)	22(1)	-4(4)	-36(2)	3(2)	
C(1,G6)	4453(3)	-559(3)	8299(2)	37(2)	34(2)	10(1)	-1(4)	5(2)	4(2)	
C(2,G6)	3770(4)	-1346(4)	8298(2)	43(3)	44(3)	21(1)	-24(5)	33(3)	-18(3)	
C(3,G6)	3290(3)	-1422(3)	7739(2)	36(2)	23(2)	16(1)	-7(4)	9(2)	-2(2)	
C(4,G6)	2799(3)	-560(3)	7602(2)	36(2)	24(2)	8(1)	2(4)	2(2)	2(2)	
C(5,G6)	3450(4)	225(3)	7666(2)	47(3)	23(2)	10(1)	-8(4)	1(2)	-6(2)	
C(6,G6)	2896(4)	1084(3)	7629(2)	63(3)	29(2)	17(1)	0(5)	-2(3)	-7(3)	
O(2,G6)	4304(4)	-2111(3)	8411(3)	111(4)	40(2)	77(2)	-48(5)	69(4)	-134(6)	
O(3,G6)	2596(3)	-2104(2)	7766(2)	48(2)	27(2)	23(1)	-32(3)	21(2)	-16(2)	
O(4,G6)	2519(2)	-620(2)	7035(1)	34(2)	28(1)	8(1)	-3(3)	-1(1)	2(2)	
O(5,G6)	3914(2)	201(2)	8200(1)	44(2)	33(2)	9(1)	6(3)	-1(1)	-4(2)	
O(6,G6)	2000(3)	1061(3)	7923(2)	75(3)	53(2)	18(1)	61(4)	-6(2)	8(3)	
C(1,P)	4952(6)	-373(5)	6188(5)	80(5)	51(4)	94(5)	-14(8)	-69(7)	43(9)	
C(2,P)	5073(7)	-701(5)	5632(3)	154(8)	47(3)	30(2)	-4(10)	7(4)	4(7)	
C(3,P)	5171(8)	-1669(5)	5699(3)	211(11)	44(3)	25(2)	22(11)	3(4)	-15(8)	
C(4,P)	5241(9)	-1845(5)	6318(3)	220(12)	53(4)	25(2)	-22(12)	-2(4)	-3(8)	
N(P)	5065(7)	-1008(5)	6587(3)	136(7)	51(3)	25(2)	-32(9)	-3(4)	3(6)	
O(P)	4828(7)	419(4)	6311(4)	209(9)	58(3)	112(4)	18(10)	-37(7)	92(11)	
O(W1)	5024(3)	1147(3)	9344(2)	47(2)	62(2)	18(1)	-4(4)	2(2)	-6(2)	
O(W2)	77(4)	1020(3)	7534(2)	88(3)	73(3)	18(1)	-30(5)	-13(3)	23(3)	
O(W3)	41(4)	1623(4)	4675(2)	88(4)	101(4)	26(1)	-1(7)	12(4)	-8(4)	
O(W4A)	239(4)	2364(4)	6749(2)	60(4)	43(3)	19(1)	6(5)	3(3)	-14(3)	0.7
O(W4B)	-114(12)	3259(16)	7189(8)	66(11)	162(18)	33(4)	-21(26)	31(16)	18(12)	0.3
O(W5A)	-322(10)	3213(8)	3088(5)	94(9)	68(7)	28(3)	11(14)	36(8)	10(9)	0.4
O(W5B)	622(7)	3241(6)	4253(4)	109(7)	81(6)	41(3)	-66(11)	19(7)	-39(8)	0.6

TABLE 2. FRACTIONAL COORDINATES ($\times 10^3$) AND ISOTROPIC TEMPERATURE FACTORS (B/Å^2) FOR HYDROGEN ATOMS

α-Cyclodextrin-DMF complex

	x	y	z	B		x	y	z	B
H(C1,G1)	109(4)	-47(4)	730(2)	2.6	H(C6BA,G4)	873(6)	143(5)	649(3)	3.0
H(C2,G1)	50(4)	-123(4)	643(2)	2.8	H(C6BB,G4)	754(6)	119(5)	682(3)	3.0
H(C3,G1)	266(4)	-131(4)	608(2)	2.3	H(O2,G4)	801(4)	-182(4)	492(2)	2.8
H(C4,G1)	95(4)	-18(4)	562(2)	2.3	H(O3,G4)	830(4)	-200(4)	680(2)	2.9
H(C5,G1)	281(4)	36(4)	629(2)	2.8	H(O6B,G4)	701(6)	225(5)	631(3)	3.3
H(C6A,G1)	233(5)	149(4)	563(3)	4.2	H(C1,G5)	876(4)	-12(4)	746(2)	2.3
H(C6B,G1)	200(5)	185(4)	629(3)	4.2	H(C2,G5)	811(4)	-99(4)	823(2)	2.4
H(O2,G1)	110(5)	-250(4)	667(3)	3.4	H(C3,G5)	646(4)	-157(4)	752(2)	2.4
H(O3,G1)	171(4)	-171(4)	524(2)	2.9	H(C4,G5)	626(4)	-35(4)	847(2)	2.4
H(O6,G1)	31(5)	100(5)	571(3)	4.9	H(C5,G5)	615(4)	20(4)	728(2)	2.5
H(C1,G2)	129(4)	22(4)	483(2)	2.4	H(C6A,G5)	634(5)	170(4)	766(2)	3.4
H(C2,G2)	206(4)	-50(4)	397(2)	2.3	H(C6B,G5)	524(5)	115(4)	782(2)	3.4
H(C3,G2)	362(4)	-109(4)	475(2)	2.1	H(O2,G5)	836(5)	-218(4)	779(2)	2.9
H(C4,G2)	376(4)	23(4)	382(2)	1.9	H(O3,G5)	604(5)	-198(4)	820(3)	3.6
H(C5,G2)	387(4)	60(4)	506(2)	2.3	H(O6,G5)	670(5)	168(4)	850(3)	4.0
H(C6A,G2)	475(5)	165(4)	454(2)	3.5	H(C1,G6)	486(4)	-40(4)	873(2)	2.5
H(C6B,G2)	357(5)	217(4)	470(2)	3.5	H(C2,G6)	313(5)	-110(4)	868(2)	3.4
H(O2,G2)	102(4)	-130(4)	449(2)	2.9	H(C3,G6)	383(4)	-157(4)	749(2)	2.9
H(O3,G2)	367(4)	-200(4)	418(2)	2.9	H(C4,G6)	214(4)	-46(4)	788(2)	2.3
H(O6,G2)	326(5)	222(4)	382(3)	4.1	H(C5,G6)	402(4)	23(4)	737(2)	2.5
H(C1,G3)	519(4)	32(4)	358(2)	2.3	H(C6A,G6)	334(5)	167(4)	781(2)	3.6
H(C2,G3)	677(4)	-61(4)	352(2)	2.1	H(C6B,G6)	277(5)	122(4)	719(2)	3.6
H(C3,G3)	622(4)	-119(4)	465(2)	2.3	H(O2,G6)	462(6)	-221(5)	819(3)	5.4
H(C3,G3)	794(4)	-9(4)	435(2)	2.0	H(O3,G6)	233(5)	-221(4)	750(2)	3.8
H(C5,G3)	609(4)	60(4)	493(2)	2.1	H(O6,G6)	173(5)	118(4)	830(3)	4.5
H(C6A,G3)	745(4)	148(4)	513(2)	2.9	H(1,W1)	516(5)	117(4)	902(3)	4.8
H(C6B,G3)	682(4)	206(4)	464(2)	2.9	H(2,W1)	541(5)	116(5)	963(3)	4.8
H(O2,G5)	502(4)	-149(4)	372(2)	2.2	H(1,W2)	74(6)	116(5)	770(3)	5.7
H(O3,G3)	699(4)	-220(4)	428(2)	2.6	H(2,W2)	-31(5)	116(5)	782(3)	5.7
H(O6,G3)	802(5)	177(4)	403(3)	3.8	H(1,W3)	6(6)	144(5)	499(3)	6.1
H(C1,G4)	895(4)	-7(4)	496(2)	2.1	H(2,W3)	-29(6)	200(5)	476(3)	6.1
H(C2,G4)	961(4)	-96(4)	573(2)	2.3	H(1,W4A)	104(6)	261(6)	683(3)	4.4
H(C3,G4)	746(4)	-136(4)	606(2)	2.1	H(2,W4A)	-67(6)	247(6)	672(3)	4.4
H(C4,G4)	903(4)	-18(4)	663(2)	2.0	H(1,W5A)	-34(8)	370(7)	349(4)	5.3
H(C5,G4)	709(4)	25(4)	605(2)	2.1	H(2,W5A)	36(8)	300(7)	319(4)	5.3

α-Cyclodextrin-2-pyrrolidone complex

	x	y	z	B		x	y	z	B
H(C1,G1)	110(4)	-45(4)	725(2)	2.6	H(C4,G4)	903(4)	-21(3)	660(2)	1.9
H(C2,G1)	44(4)	-116(4)	643(2)	2.7	H(C5,G4)	719(4)	25(3)	600(2)	2.1
H(C3,G1)	260(4)	-113(4)	608(2)	2.4	H(C6A,G4)	730(6)	122(5)	680(3)	3.4
H(C4,G1)	97(4)	-12(3)	556(2)	2.4	H(C6B,G4)	870(6)	149(6)	651(3)	3.4
H(C5,G1)	276(4)	39(4)	629(2)	3.0	H(O2,G4)	832(4)	-180(4)	503(2)	2.7
H(C6A,G1)	229(5)	150(4)	559(2)	4.2	H(O3,G4)	866(4)	-226(4)	621(2)	2.7
H(C6B,G1)	206(5)	179(4)	628(2)	4.2	H(C1,G5)	874(4)	-12(3)	741(2)	2.1
H(O2,G1)	126(4)	-247(4)	667(2)	3.1	H(C2,G5)	807(4)	-105(3)	822(2)	2.1
H(O3,G1)	173(4)	-169(4)	523(2)	3.0	H(C3,G5)	642(4)	-154(4)	743(2)	2.5
H(O6,G1)	60(5)	165(4)	602(3)	4.9	H(C4,G5)	625(4)	-36(4)	844(2)	2.3
H(C1,G2)	129(4)	19(4)	478(2)	2.9	H(C5,G5)	626(4)	19(4)	721(2)	2.5
H(C2,G2)	209(4)	-48(3)	394(2)	2.3	H(C6A,G5)	632(4)	167(4)	762(2)	3.5
H(C3,G2)	360(4)	-109(3)	476(2)	2.2	H(C6B,G5)	534(4)	118(4)	777(2)	3.5
H(C4,G2)	376(4)	16(3)	380(2)	1.9	H(O2,G5)	830(4)	-183(4)	719(2)	2.9
H(C5,G2)	380(4)	60(4)	504(2)	2.4	H(O3,G5)	665(4)	-182(4)	846(2)	3.6
H(C6A,G2)	479(4)	166(4)	450(2)	3.5	H(O6,G5)	669(5)	152(4)	864(2)	4.0
H(C6B,G2)	356(4)	214(4)	465(2)	3.5	H(C1,G6)	481(4)	-44(4)	869(2)	2.5
H(O2,G2)	133(4)	-128(4)	432(2)	2.8	H(C2,G6)	320(4)	-125(4)	863(2)	3.3
H(O3,G2)	330(4)	-131(4)	352(2)	2.7	H(C3,G6)	382(4)	-156(4)	741(2)	2.8
H(O6,G2)	299(5)	201(4)	372(3)	4.5	H(C4,G6)	221(4)	-50(3)	787(2)	2.2
H(C1,G3)	517(4)	26(3)	356(2)	2.1	H(C5,G6)	395(4)	19(4)	731(2)	2.5
H(C2,G3)	673(4)	-62(3)	352(2)	2.1	H(C6A,G6)	331(5)	163(4)	779(2)	3.6
H(C3,G3)	620(4)	-121(3)	466(2)	2.0	H(C6B,G6)	278(4)	123(4)	718(2)	3.6
H(C4,G3)	789(4)	-9(3)	430(2)	1.8	H(O2,G6)	406(6)	-276(5)	847(3)	7.9
H(C5,G3)	610(4)	65(3)	491(2)	2.0	H(O3,G6)	235(4)	-214(4)	734(2)	3.5
H(C6A,G3)	745(4)	148(4)	507(2)	2.7	H(O6,G6)	231(5)	83(4)	833(3)	4.7
H(C6B,G3)	681(4)	205(4)	458(2)	2.7	H(1,W1)	536(5)	116(4)	901(2)	4.3
H(O2,G3)	528(4)	-153(3)	395(2)	2.1	H(2,W1)	537(5)	151(4)	968(3)	4.3
H(O3,G3)	705(4)	-218(4)	430(2)	2.6	H(1,W2)	-31(5)	128(5)	779(3)	5.8
H(O6,G3)	802(4)	168(4)	402(2)	3.7	H(2,W2)	-28(5)	129(5)	718(3)	5.8
H(C1,G4)	892(4)	1(3)	496(2)	2.1	H(1,W3)	7(5)	167(5)	502(3)	6.4
H(C2,G4)	960(4)	-96(3)	567(2)	2.4	H(1,W4)	36(7)	279(6)	677(4)	4.2
H(C3,G4)	753(4)	-133(3)	603(2)	2.2					

Description and Discussion of the Structure

The atom numbering for α-CDx in both complexes (Figs. 1 and 2) is the same as that used in other complexes with the isomorphous structure.

Structure of α-CDx. Average bond distances and bond angles over six glucose residues in the α-CDx moiety are shown in Fig. 3. The corresponding distances and angles in the both complexes are in good agreement. No significant differences were observed when they were compared with those found in the α-CDx complexes with *p*-nitrophenol and *p*-hydroxybenzoic acid.[5] The primary hydroxyl group in the G4 residue is statistically disordered (Figs. 1 and 2), and shows *gauche-gauche* and *gauche-trans* conformations, while other primary hydroxyl groups are in the *gauche-*

gauche conformation. A similar disordered conformation of the primary hydroxyl group has been found in other α-CDx complexes[1,2,5] isomorphous to these complexes, although the shape and size of the guest molecule are quite different. The C(6,G4)–O(6B,G4) bond is oriented to the inside of the α-CDx ring, but shows no short contact with the included guest molecule. Therefore, the disorder of the G4 hydroxyl group may not be caused by the inclusion of the guest molecule, but by the packing requirement.

The geometry of the α-CDx ring is given in Tables 3—5. The O(4)···O(4) distances between adjacent glucose residues indicate that the deformation of the pyranose ring is slightly smaller than that found in the complexes with *p*-nitrophenol (4.016—4.493 Å) and *p*-hydroxybenzoic acid (4.053—4.509 Å).[5] The torsion-angle indices[9] (see Table 3) also show a similar tendency: they are 111.4—148.1° in the *p*-nitrophenol complex and 108.9—145.9° in the *p*-hydroxybenzoic acid complex. Between the O(4)···O(4) distances and

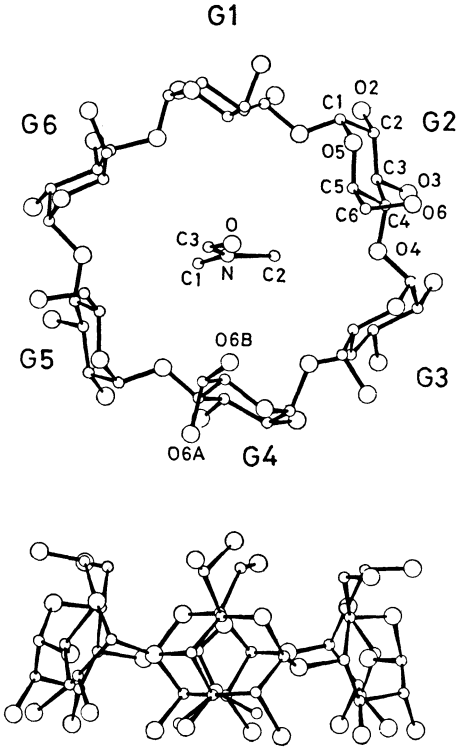

Fig. 1. Structure and numbering scheme of the α-cyclodextrin–*N*,*N*-dimethylformamide complex. O6A and O6B indicate the disordered hydroxyl oxygen atom.

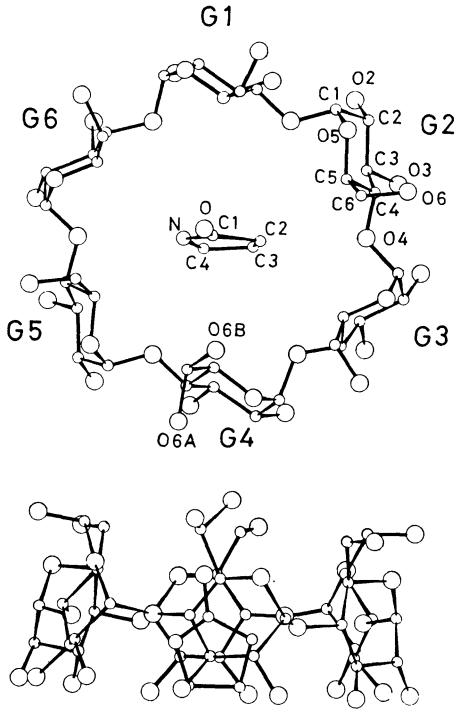

Fig. 2. Structure and numbering scheme of the α-cyclodextrin–2-pyrrolidone complex. O6A and O6B indicate the disordered hydroxyl oxygen atom.

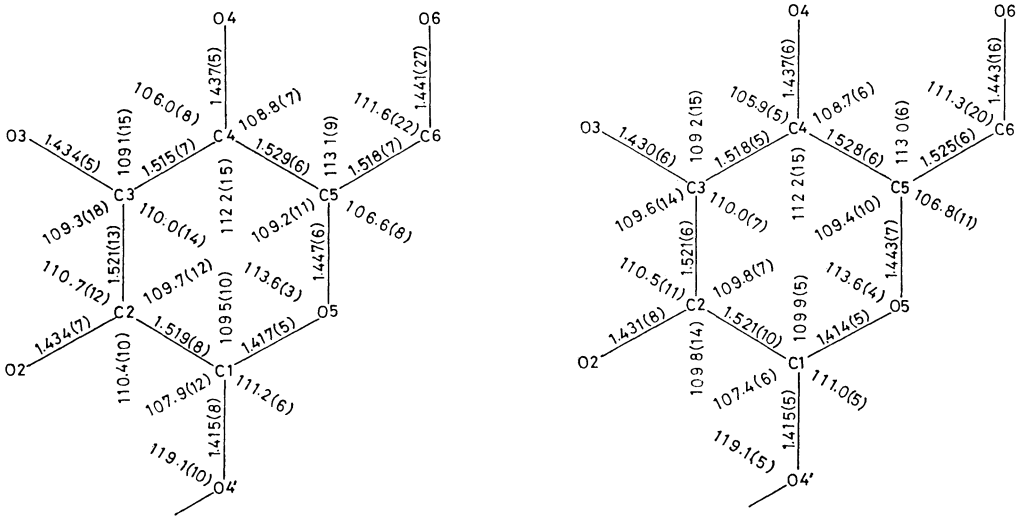

Fig. 3. Average bond distances (l/Å) and angles (ϕ/°) for the glucose residue. The standard deviations were estimated according to the equation $\sigma=[\sum_{i=1}^{6}(x_i-\bar{x})^2/5]^{1/2}$, Where x_i referes to the bond distances or angles in the i-th residue and $\bar{x}$ is the average value.

the torsion-angle index there existed a linear correlation, which was also found in other α-CDx complexes having the isomorphous structure.

The diagonal distances between glycosidic oxygen atoms (8.231—8.906 Å in the DMF complex and 8.294—8.735 Å in the PRD complex) show the distorsion of the α-CDx ring from a regular hexagonal symmetry. The longest diagonal is found along the molecular plane of the guest molecule. The deformation of the α-CDx ring in both complexes is less than that observed in the *p*-nitrophenol and *p*-hydroxybenzoic acid complexes because of the smaller size of the guest molecule. The macro-cyclic conformation of α-CDx ring has usually been described in terms of the conformation angle involving the glycosidic oxygen atoms. Owing to the ring structure of α-CDx, however, the conformation angle is found in a relatively restricted region, and does not seem to be sensitive to the conformational change. The deformation of the α-CDx ring apparently has a much greater effect on the tilt of the glucose residue against the α-CDx molecular plane. Since the planarity of the plane defined by six O(4) atoms is fairly good, in spite of the deformation of the α-CDx ring (Table 4), the tilt angle between the O(4) plane and the plane through O(4′), C(1), C(4), and O(4) for each glucose residue was calculated. These tilt-angles (Table 5) show that the G1 residue is almost perpendicular to the O(4) plane while the G5 residue is most tilted. The standard deviation for the average tilt-angle of the G6 residue is about twice as large as the standard deviation of other residues, indicating that the tilt of the G6 residue is most affected by the guest molecule.

Table 3. Selected geometrical data for α-cyclodextrin

I. Distances between glycosidic oxygen atom (l/Å)[a]	DMF complex	PRD complex
i) O(4)···O(4) distances between adjacent glucose residues		
O(4,G1)···O(4,G6)	4.347	4.300
O(4,G1)···O(4,G2)	4.201	4.201
O(4,G2)···O(4,G3)	4.110	4.131
O(4,G3)···O(4,G4)	4.439	4.399
O(4,G4)···O(4,G5)	4.212	4.205
O(4,G5)···O(4,G6)	4.190	4.199
ii) Diagonal O(4)···O(4) distances		
O(4,G1)···O(4,G4)	8.231	8.294
O(4,G2)···O(4,G5)	8.906	8.735
O(4,G3)···O(4,G6)	8.329	8.384

II. Torsion-angle index (ϕ/°)[b] Residue	DMF complex	PRD complex
G1	121.1	124.7
G2	131.6	132.3
G3	141.9	138.9
G4	112.6	115.6
G5	134.6	133.6
G6	144.7	135.0

a) Estimated standard deviations are in the range from 0.004 to 0.006 Å. b) The torsion-angle index is defined as follows: $|\phi(C(1)\text{-}C(2))| + |\phi(C(2)\text{-}C(3))| + |\phi(C(5)\text{-}O(5))| + |\phi(O(5)\text{-}C(1))| - |\phi(C(3)\text{-}C(4))| - |\phi(C(4)\text{-}C(5))|$, when the conformation angle of C(1)-C(2)-C(3)-C(4) is expressed as ϕ(C(2)-C(3)).

α-CDx - Guest Interaction. Figure 4 shows bond distances and angles in DMF and PRD, and intermolecular atomic contacts between α-CDx and these guests. The bond distances and angles in PRD are in good agreement with those found in (*S*)-5-iodomethyl-2-pyrrolidone and (*S*)-5-oxo-2-pyrrolidinecarboxamide.[10] On the other hand, a rather short C(3)–O distance (1.10 Å) and large C(3)–N–C(2) angle (133°) are found in DMF. This may be due to the large thermal motion of the DMF molecule. A similar effect has

Table 4. Least-squares planes and deviations of atoms from the plane (l/Å)
An asterisk indicates the atom not included in the plane.

I. α-Cyclodextrin-DMF complex

i) The plane through the DMF molecule.
$0.979X+0.178Y-0.097Z=5.119$

C(1,DF)	0.020	N(DF)	−0.023
C(2,DF)	0.003	O(DF)	0.027
C(3,DF)	−0.027		

ii) The plane through six O(4) atoms.
$0.017X+0.996Y+0.091Z=0.811$

O(4,G1)	0.091	O(4,G4)	0.115
O(4,G2)	0.046	O(4,G5)	0.020
O(4,G3)	−0.148	O(4,G6)	−0.125

iii) Deviations of atoms from the plane through C(2), C(3), C(5), and O(5).

Residue	C(1)*	C(2)	C(3)	C(4)*	C(5)	O(5)
G1	−0.666	−0.015	0.015	0.675	−0.016	0.016
G2	−0.688	−0.003	0.003	0.624	−0.003	0.003
G3	−0.704	−0.001	0.001	0.586	−0.001	0.001
G4	−0.640	−0.026	0.025	0.696	−0.027	0.028
G5	−0.697	−0.026	0.024	0.584	−0.025	0.027
G6	−0.736	−0.027	0.025	0.606	−0.027	0.029

II. α-Cyclodextrin-PRD complex

i) The plane through the PRD molecule.
$0.988X+0.153Y+0.015Z=6.936$

C(1,P)	−0.024	C(4,P)	0.030
C(2,P)	0.045	N(P)	−0.003
C(3,P)	−0.046	O(P)	−0.002

ii) The plane through six O(4) atoms.
$0.017X+0.995Y+0.096Z=0.876$

O(4,G1)	0.097	O(4,G4)	0.103
O(4,G2)	0.030	O(4,G5)	0.020
O(4,G3)	−0.129	O(4,G6)	−0.122

iii) Deviations of atoms from the plane through C(2), C(3), C(5), and O(5).

Residue	C(1)*	C(2)	C(3)	C(4)*	C(5)	O(5)
G1	−0.669	−0.010	0.010	0.665	−0.010	0.011
G2	−0.695	−0.002	0.002	0.618	−0.002	0.002
G3	−0.696	−0.001	0.001	0.599	−0.001	0.001
G4	−0.645	−0.026	0.025	0.692	−0.027	0.028
G5	−0.678	−0.025	0.024	0.591	−0.025	0.027
G6	−0.701	−0.005	0.005	0.606	−0.006	0.006

Table 5. Angles (ϕ/°) made between the plane through six O(4) atoms and the plane through O(4′), C(1), C(4), and O(4)
Figures in parentheses are standard deviations.

Residue	*p*-IAN[a]	*p*-IPH[b]	*p*-NPH[c]	*p*-HBA[d]	DMF	PRD	Average
G1	2.1	3.9	3.8	3.9	5.7	5.5	4.2(12)
G2	9.7	11.2	10.1	11.3	12.1	13.5	11.3(14)
G3	10.3	11.8	11.3	11.0	11.7	9.7	11.0(8)
G4	12.1	12.1	14.4	12.1	12.4	14.4	12.9(12)
G5	15.6	15.9	17.0	16.1	15.4	18.1	16.4(10)
G6	15.1	10.9	10.7	7.5	14.2	12.2	11.7(27)

a) *p*-Iodoaniline.[1] b) *p*-Iodophenol.[2] c) *p*-Nitrophenol.[5] d) *p*-Hydroxybenzoic acid.[5]

been observed in the α-CDx complexes with a small guest molecule.[11–13] DMF and PRD show good planarity: the maximum deviation from the plane is 0.046 Å in PRD and 0.027 Å in DMF.

In the α-CDx cavity, the DMF and PRD molecules are located nearly parallel to the O(4,G2)···O(4,G5) diagonal line. In the DMF complex, two methyl groups are located at the O(2), O(3) side, while the C(3) atom is nearly on the O(4) plane. The shortest intermolecular distance between DMF and α-CDx is 3.76 Å, found between O(4,G6) and C(3,DF), indicating that the DMF molecule is in van der Waals contact with the host α-CDx molecule. In the PRD complex, the C(3)–C(4) bond is nearly on the plane composed of twelve secondary hydroxyl groups, and the carbonyl oxygen atom is located at a similar position to that of the oxygen atom found in the DMF complex. Some relatively short contacts are found in the PRD complex: O(4, G2)···C(2,P) of 3.32 Å and O(4,G5)···N(P) of 3.20 Å. The O(4)···N distance indicates the formation of a weak O(4)···H–N hydrogen bond between α-CDx and PRD, since the N–H bond is oriented to the O(4,G5) atom. Thus, the PRD complex shows that the non-aromatic ring compound can be included in the α-CDx cavity.

Molecular Packing and Hydrogen Bonds. Three types of crystal structures have already been found in α-CDx complexes. The "channel-type" structure is built up by a linear stack of α-CDx molecules to form endless channels.[3,4,6,11,14] In the "cage-type"

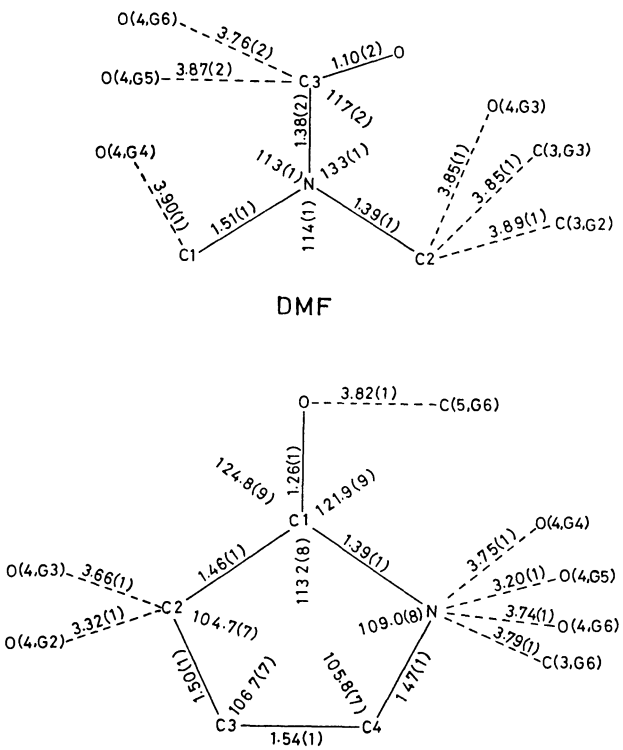

Fig. 4. Bond distances (l/Å) and angles (ϕ/°) in *N*,*N*-dimethylformamide and 2-pyrrolidone. Broken lines indicate contacts with the host α-cyclodextrin.

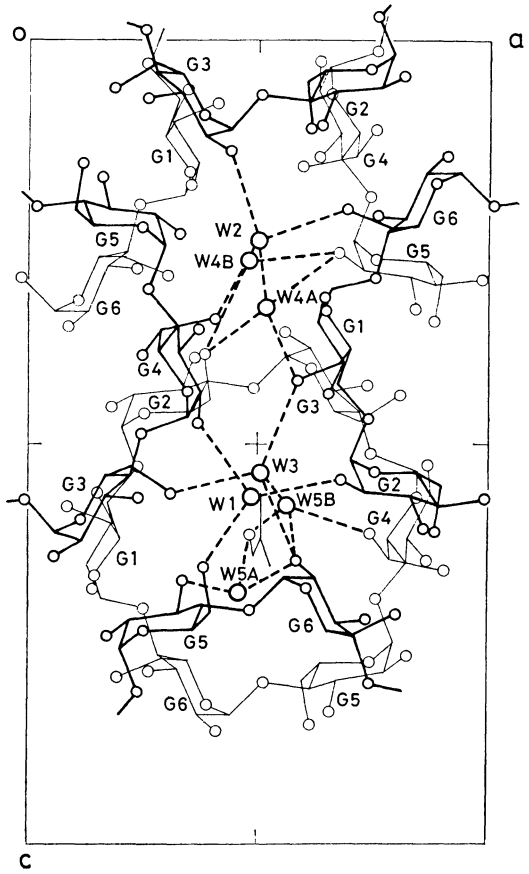

Fig. 5. A schematic drawing of the hydrogen-bond network involving water molecules in the α-cyclodextrin–*N*,*N*-dimethylformamide complex. Small circles indicate hydroxyl groups of α-cyclodextrin. Water molecules are shown by large circles.

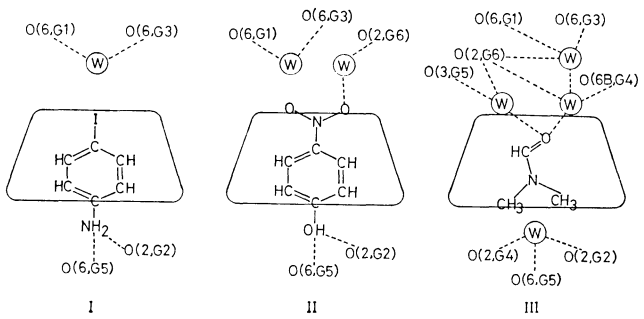

Fig. 6. A schematic drawing of the environment of the guest molecule in the α-cyclodextrin complexes with *p*-iodoaniline (I), *p*-nitrophenol (II), and *N,N*-dimethylformamide (III).

structure, α-CDx molecules are arranged in a fish-bone-like fashion, producing an isolated cavity to accommodate a guest molecule.[12,13,15–17] The DMF and PRD complexes have the "layer" structure, in which α-CDx molecules are arranged to form molecular layers in the crystal (Fig. 5).[1,2,5,8]

Hydrogen-bond distances and angles are given in Table 6, and the hydrogen-bonding network involving water molecules is shown in Fig. 5. Several differences are found in the hydrogen-bonding contacts compared with other complexes having the "layer" structure. In the DMF and PRD complexes, five intramolecular O(2)···O(3) hydrogen bonds are observed, but unlike the complexes with *p*-nitrophenol and *p*-hydroxybenzoic acid,[5] the G5 residue forms no hydrogen bond with the G6. These residues seem to be linked by the O(2)···water···O(3) hydrogen bond. Significantly short intermolecular distances are found in the contacts of O(2,G6)···W5, 2.371 Å (O(W5B)) in the DMF complex and 2.340 Å (O(W5A)) in the PRD complex. These may be due to errors caused at the stage of the structure refinement, owing to the low population of the disordered water and the relatively large thermal motion of O(2,G6) (5.4 Å^2 in the DMF complex and 7.9 Å^2 in the PRD complex) compared with the other secondary hydroxyl oxygen atoms (2.1—3.8 Å^2). A similar short contact has been also found in the α-CDx–*p*-nitrophenol complex.[5]

In a layer composed of α-CDx molecules, hydrogen bonds are found between G2 and G6, and G3 and G5. No hydrogen bond was found between G1 and G4, although they face each other (Fig. 5). The adjacent layers are also linked by G1···G3 and G2···G4 hydrogen bonds. The DMF and PRD complexes have different hydrogen-bonding directions. The O(3,G2)–H···O(3,G4)–H···O(2,G5) linkage in the DMF complex is changed to the O(3,G2)···H–O(3,G4)···H–O(2,G5) linkage in the PRD complex.

In the α-CDx complexes with *p*-iodoaniline,[1] *p*-iodophenol,[2] *p*-nitrophenol, and *p*-hydroxybenzoic

Table 6. Hydrogen-bond distances (*l*/Å), angles (φ/°), and intermolecular oxygen-oxygen contacts (*l*/Å) less than 3.0 Å[a]

α-CDx DMF complex			Distance O-H	H···O	O···O	Angle O-H···O
O(2,G1)-H	O(2,G3)	(h)	0.93	1.89	2.795	165
O(3,G1)-H	O(2,G2)		1.01	1.74	2.738	169
O(2,G2)-H	O(W1)	(c)	1.16	1.51	2.663	172
O(3,G2)-H	O(3,G4)	(h)	1.04	2.29	2.739	104
O(6,G2)-H	O(6B,G4)	(g)	1.04	1.72	2.727	160
O(2,G3)-H	O(3,G2)		0.88	1.97	2.845	173
O(3,G3)-H	O(3,G1)	(i)	1.01	1.68	2.674	168
O(6,G3)-H	O(3,G5)	(d)	0.98	1.87	2.776	152
O(2,G4)-H	O(3,G3)		1.33	1.82	3.080	157
O(3,G4)-H	O(2,G5)		1.04	1.89	2.887	159
O(6B,G4)-H	O(W5B)	(f)	0.97	2.38	2.636	95
O(6B,G4)-H	O(2,G6)	(j)	0.97	1.96	2.873	156
O(2,G5)-H	O(W4B)	(k)	0.69	2.61	2.664	87
O(3,G5)-H	O(W5A)	(b)	0.85	2.16	2.656	117
O(6,G5)-H	O(3,G3)	(e)	0.96	2.24	2.802	116
O(2,G6)-H	O(W5A)	(b)	1.16	1.86	2.659	121
O(3,G6)-H	O(2,G1)		0.87	2.07	2.899	159
O(6,G6)-H	O(3,G2)	(b)	1.01	1.70	2.704	177
O(W1)-H(1)	O(6,G5)		0.91	1.94	2.715	142
O(W1)-H(2)	O(2,G4)	(e)	1.94	2.00	2.877	155
O(W2)-H(1)	O(6,G6)		1.06	1.80	2.846	166
O(W2)-H(2)	O(2,G3)	(b)	0.89	2.09	2.930	159
O(W3)-H(1)	O(6,G1)		0.82	2.25	2.949	143
O(W3)-H(2)	O(W5B)		0.89	2.52	2.725	94
O(W3)-H(2)	O(6,G3)	(a)	0.89	2.49	2.813	102
O(W4A)-H(1)	O(6,G2)	(g)	1.17	2.02	2.791	114
O(W4A)-H(1)	O(2,G5)	(j)	1.17	1.86	2.821	136
O(W5A)-H(1)	O(DF)	(g)	1.10	1.93	2.984	159
O(6,G2)	O(W4B)	(f)			2.823	
O(6,G2)	O(6A,G4)	(g)			2.931	
O(2,G6)	O(W5B)	(b)			2.371	
O(2,G6)	O(W3)	(b)			2.953	
O(W2)	O(W4A)				2.818	
O(W2)	O(6A,G4)	(a)			2.803	
O(W4A)	O(6,G1)				2.838	
O(W5B)	O(DF)	(g)			2.905	

α-CDx-2-pyrrolidone complex			Distance O-H	H···O	O···O	Angle O-H···O
O(2,G1)-H	O(2,G3)	(h)	0.78	2.00	2.775	172
O(3,G1)-H	O(2,G2)		0.99	1.77	2.739	165
O(6,G1)-H	O(W4A)		0.75	2.14	2.870	164
O(2,G2)-H	O(W1)	(c)	0.91	1.88	2.668	143
O(6,G2)-H	O(6B,G4)	(g)	1.24	1.81	2.738	127
O(2,G3)-H	O(3,G2)		0.94	2.24	2.810	118
O(3,G3)-H	O(3,G1)	(i)	0.94	1.76	2.699	175
O(2,G4)-H	O(3,G3)		0.80	2.29	3.042	158
O(3,G4)-H	O(3,G2)	(i)	0.79	2.02	2.736	151
O(2,G5)-H	O(3,G4)		0.98	1.97	2.910	161
O(6,G5)-H	O(3,G3)	(e)	0.94	1.99	2.877	160
O(2,G6)-H	O(W5B)	(b)	1.07	2.08	2.686	113
O(2,G6)-H	O(W5A)	(b)	1.07	2.09	2.340	89
O(3,G6)-H	O(2,G1)		1.07	1.87	2.878	157
O(6,G6)-H	O(3,G2)	(b)	1.14	2.22	2.706	103
O(W1)-H(1)	O(6,G5)		0.93	1.80	2.727	170
O(W1)-H(2)	O(2,G4)	(e)	1.10	1.81	2.862	159
O(W2)-H(1)	O(2,G3)	(b)	0.92	2.07	2.893	147
O(W2)-H(2)	O(6A,G4)	(a)	1.09	1.81	2.876	166
O(W2)-H(2)	O(W4A)		1.09	2.08	2.828	124
O(W3)-H(1)	O(6,G1)		0.83	2.14	2.888	149
O(W4A)-H(1)	O(2,G5)	(j)	0.69	2.48	2.841	112
O(W4A)-H(1)	O(6,G2)	(g)	0.69	2.68	2.781	91
O(6,G2)	O(W4B)	(f)			2.792	
O(6,G2)	O(6A,G4)	(g)			2.904	
O(6B,G4)	O(W5B)	(f)			2.679	
O(2,G5)	O(W4B)	(k)			2.611	
O(3,G5)	O(W5A)	(b)			2.543	
O(6,G6)	O(W2)				2.828	
O(W3)	O(W5B)				2.825	
O(W3)	O(6,G3)	(a)			2.802	
O(W5A)	O(P)	(g)			2.571	
O(W5B)	O(P)	(g)			2.733	

Code	Symmetry operator	Code	Symmetry operator
None	x, y, z	c	1/2-x, -y, -1/2+z
a	-1+x, y, z	d	3/2-x, -y, -1/2+z
b	1/2-x, -y, z	e	3/2-x, -y, 1/2+z

Code	Symmetry operator	Code	Symmetry operator
f	1/2+x, 1/2-y, 1-z	i	1/2+x,-1/2-y, 1-z
g	-1/2+x, 1/2-y, 1-z	j	1-x, 1/2+y, 3/2-z
h	-1/2+x,-1/2-y, 1-z	k	1-x,-1/2+y, 3/2-z

a) The hydrogen bond is doubtful if the H···O distance is longer than 2.5Å or the O-H···O angle is less than 90°.

acid,[5] the guest molecules are so bulky that a part of the guest molecule protrudes from the secondary hydroxyl side of the α-CDx cavity. The environment of the guest molecule is schematically shown in Fig. 6. In the DMF complex, the open end of the primary hydroxyl side of α-CDx is blocked by two water molecules. One (W3) is located near the position found in the *p*-iodoaniline or *p*-nitrophenol complex, but the other (W5) is not found in the complexes with the aromatic guest. W3 is linked to the adjacent three α-CDx molecules. The DMF molecule is so small that the vacant space is filled by W5, which is statistically disordered and occupies two sites. W1 blocks the secondary hydroxyl side of the α-CDx cavity, but it is replaced by the amino or hydroxyl group of the guest molecule in the complexes with *p*-iodoaniline and *p*-nitrophenol. W2, W4A, and W4B are found at the same position as those found in other α-CDx complexes with the "layer" structure. They are arranged in the space elongated along the two-fold screw axis perpendicular to the α-CDx molecular plane (Fig. 5).

So far, it has been considered that the "layer" structure is formed when the guest molecule is too bulky to be enclosed in the α-CDx cavity. But, the DMF and PRD complexes show that a complex with a small guest molecule can also form the "layer" structure. α-CDx crystallized from an ethanol–water solution may also have a layer structure, since the lattice dimensions are almost the same as those of the complexes with the "layer" structure; $a=13.39$, $b=15.49$, $c=24.06$ Å, and the space group $P2_12_12_1$.[18] The α-CDx crystal obtained from a methanol–water or 1-propanol–water solution gives the "cage-type" structure.[15,17] It is very interesting to speculate why the ethanol complex does not form the "cage-type" structure.

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References

1) K. Harata, *Bull. Chem. Soc. Jpn.*, **48**, 2409 (1975).
2) K. Harata, *Carbohydr. Res.*, **48**, 265 (1976).
3) K. Harata, *Bull. Chem. Soc. Jpn.*, **49**, 1493 (1976).
4) K. Harata, *Bull. Chem. Soc. Jpn.*, **49**, 2066 (1976).
5) K. Harata, *Bull. Chem. Soc. Jpn.*, **50**, 1416 (1977).
6) K. Harata, H. Uedaira, and J. Tanaka, *Bull. Chem. Soc. Jpn.*, **51**, 1627 (1978).
7) M. Otagiri, K. Ikeda, K. Uekama, O. Ito, and M. Hatano, *Chem. Lett.*, **1974**, 679.
8) K. Harata, *Bull. Chem. Soc. Jpn.*, **51**, 1644 (1978).
9) A. D. French and V. G. Murphy, *Carbohydr. Res.*, **27**, 391 (1973).
10) J. A. Molin-Case, E. Fleischer, and D. W. Urry, *J. Am. Chem. Soc.*, **92**, 4728 (1970).
11) K. Harata, *Bull. Chem. Soc. Jpn.*, **50**, 1259 (1977).
12) W. Saenger, R. K. McMullan, J. Fayos, and D. Mootz, *Acta Crystallogr., Sect. B*, **30**, 2019 (1974).
13) B. Hingerty and W. Saenger, *J. Am. Chem. Soc.*, **98**, 3357 (1976).
14) A. Hybl, R. E. Rundle, and D. E. Williams, *J. Am. Chem. Soc.*, **87**, 2779 (1965).
15) R. K. McMullan, W. Saenger, J. Fayos, and D. Mootz, *Carbohydr. Res.*, **31**, 211 (1973).
16) P. C. Manor and W. Saenger, *J. Am. Chem. Soc.*, **96**, 3630 (1974).
17) W. Saenger and M. Noltemeyer, *Chem. Ber.*, **109**, 503 (1976).
18) D. French and R. E. Rundle, *J. Am. Chem. Soc.*, **64**, 1651 (1942).