The Structure of the Cyclodextrin Complex. II. The Crystal Structure of α-Cyclodextrin-Methyl Orange (2 : 1) Complex

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α-Cyclodextrin(α-CDx) forms 2 : 1 complexes with Methyl Orange sodium salt (MONa) and Methyl Orange potassium salt (MOK). The structures were investigated by the X-ray method. The crystals of both complexes belongs to the orthorhombic space group $P2_12_12$ with $Z=2$; the cell dimensions are $a=22.099(6)$, $b=16.359(3)$, and $c=8.296(1)$ Å for the MONa complex, and $a=22.120(4)$, $b=16.419(4)$, and $c=8.292(1)$ Å for the MOK complex. Weak streaks were observed between the layer lines in the oscillation photographs around the c* axis. The structures were determined by using 1566 reflections for the MONa complex and 2544 reflections for the MOK complex, and were refined by the least-squares method to the final R-values of 0.11 and 0.10 respectively. α-CDx is a doughnut-shaped molecule with a large cavity. The crystals have channel structures built up by the stacking of α-CDx rings along the c axes. The Methyl Orange anions are located in the channel with a statistical disorder of four different arrangements. The azo group and the benzene ring are included in the cavity of α-CDx, but the dimethylamino and sulfonato groups protrude from the cavity and are in contact with the adjacent α-CDx rings. The azo group is located at the "neck" of the cavity. The sulfonato group is hydrogen-bonded to the primary hydroxyl groups of α-CDx. No significant structural difference was observed between the MONa complex and the MOK complex.

Cyclodextrins, which are cyclic oligosaccharides consisting of α-1,4-linked D-glucose residues, have a cavity in the center of the molecule and form inclusion complexes with a number of organic compounds. Lautsch and his co-workers have used cyclodextrin-dye complexes as an enzyme model.[1] Cramer *et al.*[2] have measured the rate constants and equilibrium constants for the association of α-cyclodextrin (α-CDx) with a series of azo dyes, and suggested that the dyes are enclosed in the cyclodextrin ring. They have also indicated that α-CDx and Methyl Orange can form complexes with higher stoichiometric ratio than a 1 : 1 ratio.

The crystal structures of several α-CDx complexes have been determined by X-ray analysis,[3-8] and it has been shown that the "guest" molecule is included in the cavity of α-CDx. α-CDx forms a 2 : 1 complex with Methyl Orange. The cell dimensions and the space group of Methyl Orange complex have been determined by McMullan *et al.*[9] and it has been suggested that the structure is of a channel type. The reported space group is $P2_12_12_1$, but we have found that the α-CDx-Methyl Orange complex crystallizes in the space group of $P2_12_12$, the same as that of the α-CDx-potassium acetate complex.[3] A Methyl Orange anion is longer than the depth of the cavity of α-CDx. Therefore, it is of interest to know in what manner Methyl Orange forms the complex with α-CDx. The present X-ray analysis was undertaken in order to find the geometry of the complex and the interaction between α-CDx and Methyl Orange. Both salts, sodium (MONa) and potassium (MOK), were studied in order to investigate the effect of cations in the complex structure.

Experimental

Crystals of α-CDx-Methyl Orange complexes, which were obtained by cooling a hot aqueous solution containing α-CDx and Methyl Orange with a 2 : 1 molar ratio, are orange prisms elongated along the c axis. The density was measured by the flotation method in a mixture of chloroform and hexane. On oscillation photographs around the c* axis, weak streaks were found between the layer lines, as is shown in Fig. 1. The intensity data were measured on a Rigaku AFC four-circle diffractometer with a 2θ-ω scanning mode. The crystal was enclosed in a quartz capillary with a small amount of solvent, since the crystal breaks up in air. For the MONa complex, 3108 independent reflections were obtained with a graphite monochromatized Mo$K\alpha$ radiation up to 50° in 2θ, by using a specimen with dimensions of $0.3\times0.5\times0.5$ mm, but 1542 reflections with $|F_o|<3\sigma(F)$ were considered to be unobserved. For the MOK complex, four sets of independent reflections were obtained with Cu$K\alpha$ radiation up to 120° in 2θ, by using two specimens with dimensions of $0.2\times0.4\times0.4$ mm and $0.3\times0.3\times0.4$ mm. By averaging the intensities of equivalent reflections, 2544 reflections with $|F_o|>3\sigma(F)$ were used for the structure determination. The usual LP corrections were applied, but no correction was made for absorption and extinction. The crystal data are shown in Table 1.

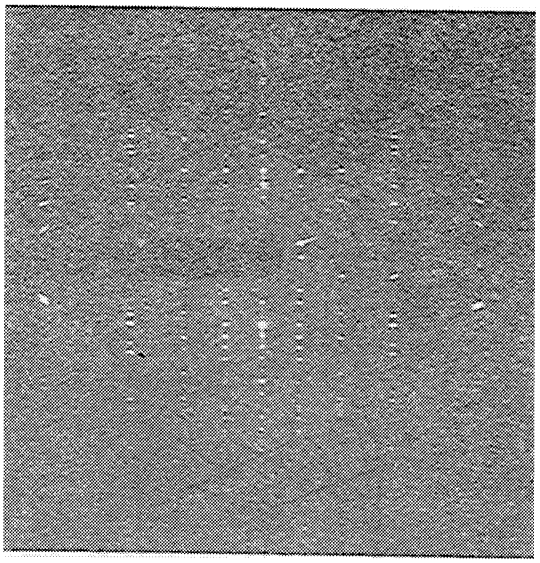

Fig. 1. An oscillation photograph around the c* axis.

TABLE 1. CRYSTAL DATA

		α-Cyclodextrin-Methyl Orange sodium salt complex $C_{36}H_{60}O_{30}\cdot 0.5C_{14}H_{14}O_3N_3SNa\cdot 9.75H_2O$	α-Cyclodextrin-Methyl Orange potassium salt complex $C_{36}H_{60}O_{30}\cdot 0.5C_{14}H_{14}O_3N_3SK\cdot 9.75H_2O$
Molecular weight		1312.2	1320.2
Cell dimensions	a	22.099(6) Å	22.120(4) Å
	b	16.359(3)	16.419(4)
	c	8.296(1)	8.292(1)
Cell volume	V	2998.9Å^3	3011.7Å^3
Space group		$P2_12_12$	$P2_12_12$
	Z	2	2
Density	D_0	1.45 g·cm^{-3}	1.48 g·cm^{-3}
	D_c	1.45	1.46

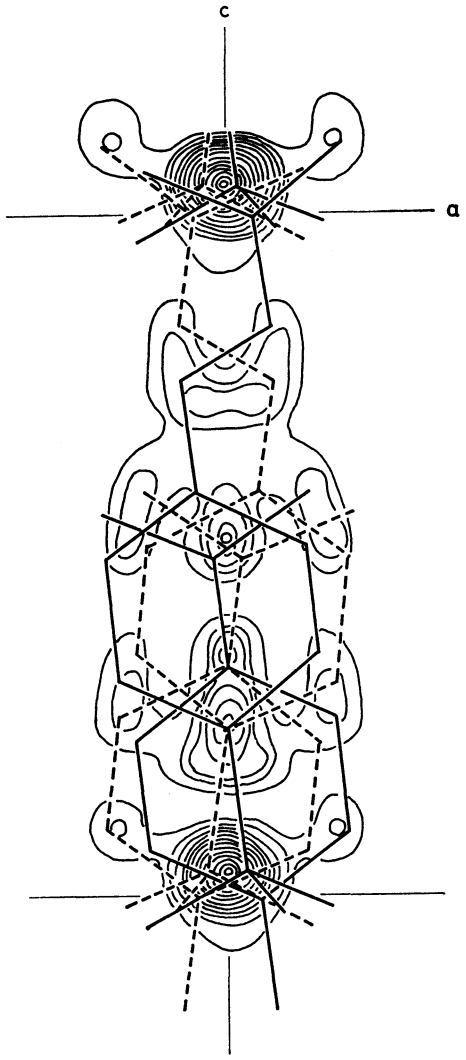

Fig. 2. The $Y=0$ section of a three-dimensional electron density map calculated by using the phases on the basis of α-cyclodextrin, showing Methyl Orange anion. The contours are at an arbitrary interval. The solid line represents a Methyl Orange anion and its shifted one overlapped in the same cell, and the broken line shows the anions related by the two-fold symmetry.

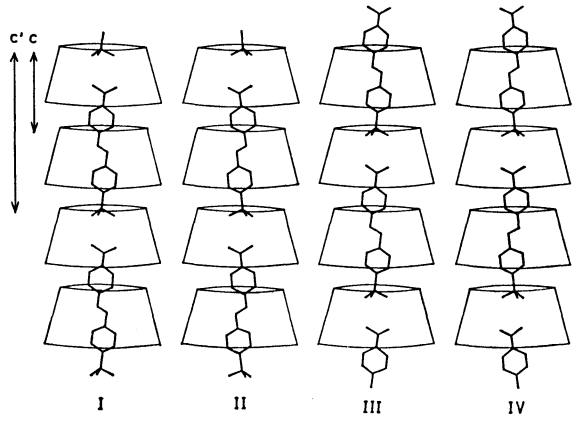

Fig. 3. Schematic drawings of the four arrangements of the Methyl Orange anion in the channel.

Determination and Refinement of the Structure

The cell dimensions of the crystals are similar to those of the α-CDx-potassium acetate complex[3] with the same space group. The potassium acetate complex gives $a=21.89$, $b=16.54$, and $c=8.30$ Å, and the space group is $P2_12_12$. Therefore, we considered that the framework of the crystal structure is the same as that of the potassium acetate complex. The positions and orientations of glucose residues were refined by the rigid-body least-squares method, starting from the same set of coordinates with the potassium acetate complex. Then, the parameters of each atom in α-CDx were refined by the block-diagonal least-squares method. At this stage, a Fourier map was calculated (Fig. 2). It showed that the Methyl Orange anion is located on the two-fold axis. The strongest peak was assigned to the sulfur atom of the sulfonato group; the arrangement of the anion was then considered to be as is shown in Fig. 2. The Methyl Orange anion is asymmetric, and in order to satisfy the two-fold symmetry required by the space group, the transposed structure must be considered. Since the length of the anion is nearly twice the c lattice unit, the shifted arrangement of anions along the c axis must be equally populated to accommodate a long molecule in a short cell. Therefore, the structure of the crystal must be

TABLE 2. FINAL ATOMIC COORDINATES AND THERMAL FACTORS ($\times 10^4$)
The anisotropic thermal 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.

α-Cyclodextrin-Methyl Orange Sodium Salt

	OC	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{23}	B_{31}
C(1,G1)	1.00	1536(8)	2422(12)	3532(23)	22(5)	55(10)	140(32)	6(12)	19(36)	14(23)
C(2,G1)	1.00	1263(7)	2842(10)	4925(22)	16(4)	34(8)	144(28)	-10(10)	2(29)	-6(20)
C(3,G1)	1.00	613(7)	2603(10)	5132(19)	21(4)	32(8)	71(22)	5(9)	9(24)	-1(17)
C(4,G1)	1.00	252(7)	2775(10)	3596(18)	21(4)	36(8)	86(23)	-14(11)	11(27)	6(19)
C(5,G1)	1.00	559(9)	2346(12)	2178(23)	25(5)	48(10)	141(31)	3(13)	15(32)	-16(23)
C(6,G1)	1.00	267(9)	2635(14)	560(22)	24(5)	86(13)	145(32)	-6(15)	-33(39)	-5(23)
O(2,G1)	1.00	1587(5)	2651(8)	6354(14)	23(3)	56(7)	115(18)	-9(8)	-14(22)	-58(14)
O(3,G1)	1.00	324(6)	3033(8)	6470(15)	26(3)	56(6)	134(20)	4(9)	-35(23)	-10(16)
O(4,G1)	1.00	-336(5)	2428(7)	3793(13)	20(3)	37(5)	105(17)	4(7)	25(19)	1(14)
O(5,G1)	1.00	1184(5)	2627(8)	2092(13)	21(3)	51(6)	106(18)	-6(8)	52(20)	-1(14)
O(6,G1)	0.65	517(10)	2237(14)	-615(20)	41(7)	76(13)	67(26)	33(17)	4(33)	-3(23)
O(6',G1)	0.35	286(22)	3304(27)	113(54)	58(17)	73(24)	266(92)	-16(34)	223(89)	-153(72)
C(1,G2)	1.00	2488(9)	-549(11)	3461(22)	31(6)	41(9)	115(29)	10(12)	-8(30)	3(25)
C(2,G2)	1.00	2642(8)	-17(12)	4881(20)	21(5)	47(9)	111(25)	-1(12)	52(34)	-17(21)
C(3,G2)	1.00	2142(8)	663(10)	5117(20)	21(5)	30(8)	88(24)	-4(10)	-9(26)	2(19)
C(4,G2)	1.00	2059(8)	1137(10)	3594(20)	25(5)	34(8)	93(25)	1(10)	25(28)	-1(21)
C(5,G2)	1.00	1993(9)	574(11)	2102(19)	27(5)	40(9)	77(23)	20(12)	12(26)	-3(21)
C(6,G2)	1.00	2094(10)	1040(14)	509(22)	39(7)	72(13)	100(30)	11(16)	14(34)	-31(24)
O(2,G2)	1.00	2645(6)	-517(7)	6316(16)	37(5)	46(6)	146(21)	9(9)	16(23)	-72(19)
O(3,G2)	1.00	2326(5)	1227(7)	6326(14)	25(3)	39(6)	98(17)	-7(7)	18(20)	-12(15)
O(4,G2)	1.00	1545(5)	1578(6)	3791(13)	22(3)	31(5)	86(16)	3(7)	15(18)	-6(13)
O(5,G2)	1.00	2443(5)	-42(8)	2054(13)	22(3)	44(6)	125(18)	6(8)	16(21)	35(14)
O(6,G2)	0.65	1957(15)	583(14)	-723(26)	91(13)	56(12)	127(38)	31(21)	-4(38)	28(41)
O(6',G2)	0.35	2597(24)	1297(28)	107(58)	65(18)	81(26)	203(82)	-56(36)	183(87)	61(68)
C(1,G3)	1.00	834(8)	-2935(11)	3544(26)	21(5)	35(9)	192(36)	13(11)	-5(34)	-1(25)
C(2,G3)	1.00	1251(8)	-2890(12)	5019(27)	15(5)	58(10)	217(37)	7(12)	77(39)	0(23)
C(3,G3)	1.00	1477(7)	-2011(11)	5173(19)	11(4)	49(9)	101(25)	-12(10)	-46(29)	25(17)
C(4,G3)	1.00	1789(7)	-1738(10)	3553(20)	16(4)	38(8)	121(26)	-7(10)	55(29)	14(20)
C(5,G3)	1.00	1359(8)	-1833(11)	2167(19)	24(5)	47(9)	67(23)	-21(12)	-32(27)	33(18)
C(6,G3)	1.00	1713(10)	-1648(14)	550(22)	31(6)	75(13)	121(30)	-16(15)	29(35)	-33(24)
O(2,G3)	1.00	929(6)	-3158(9)	6289(19)	24(4)	68(8)	26(30)	1(9)	117(31)	5(20)
O(3,G3)	1.00	1936(6)	-1983(8)	6406(14)	29(4)	56(7)	104(18)	-2(9)	17(22)	-32(16)
O(4,G3)	1.00	1890(5)	-865(7)	3802(13)	14(3)	42(5)	87(16)	-6(7)	13(18)	12(13)
O(5,G3)	1.00	1169(5)	-2698(8)	2118(13)	19(3)	55(7)	118(19)	0(8)	-25(21)	20(14)
O(6,G3)	0.55	1320(14)	-1767(19)	-576(33)	53(11)	88(18)	169(53)	-56(24)	44(55)	84(40)
O(6',G3)	0.45	2112(16)	-2132(22)	-33(52)	48(12)	75(21)	375(88)	38(27)	169(82)	182(59)
Na	0.25	1758(19)	4793(40)	629(97)	14(11)	153(43)	1332(275)	-10(37)	-125(209)	201(98)
O(W1)	1.00	3315(7)	8409(10)	671(17)	45(5)	86(9)	146(24)	34(12)	-31(27)	25(19)
O(W2)	1.00	3820(11)	1227(13)	701(21)	117(11)	116(13)	186(31)	-90(21)	60(37)	-59(33)
O(W3)	1.00	4291(14)	9747(15)	3418(31)	141(15)	125(17)	504(58)	-33(27)	99(65)	105(55)
O(W4)	1.00	663(15)	4921(17)	2936(36)	158(16)	111(15)	793(85)	-76(30)	-60(84)	-190(66)
O(W5)	0.75	1582(13)	4936(17)	967(37)	64(10)	86(14)	645(83)	35(21)	46(80)	22(60)
O(W6)	0.25	0(-)	5000(-)	149(83)	90(29)	176(52)	448(157)	126(70)	0(-)	0(-)

Hydrogen Atoms

	OC	x	y	z	B
H(1,G1)	1.00	2013	2574	3336	4.9
H(2,G1)	1.00	1318	3499	4705	3.4
H(3,G1)	1.00	588	1951	5473	2.6
H(4,G1)	1.00	193	3429	3329	3.7
H(5,G1)	1.00	539	1669	2402	4.2
H(61,G1)	0.65	337	3285	396	5.1
H(62,G1)	0.65	-229	2488	555	5.1
H(61',G1)	0.35	407	2250	-446	5.1
H(62',G1)	0.35	-218	2435	501	5.1
H(1,G2)	1.00	2774	-1093	3233	4.2
H(2,G2)	1.00	3108	234	4707	4.0
H(3,G2)	1.00	1723	359	5505	2.7
H(4,G2)	1.00	2438	1604	3414	3.5
H(5,G2)	1.00	1549	227	2212	4.3
H(61,G2)	0.65	2550	1239	404	4.7
H(62,G2)	0.65	1772	1589	491	4.7
H(61',G2)	0.35	1854	753	-502	4.7
H(62',G2)	0.35	1768	1584	484	4.7
H(1,G3)	1.00	615	-3550	3319	4.9
H(2,G3)	1.00	1662	-3260	5164	4.7
H(3,G3)	1.00	1088	-1616	5477	2.8
H(4,G3)	1.00	2214	-2073	3252	2.9
H(5,G3)	1.00	953	-1431	2377	3.3
H(61,G3)	0.55	2074	-2100	397	4.8
H(62,G3)	0.55	1873	-1008	524	4.8
H(61',G3)	0.45	1895	-1019	554	4.8
H(62',G3)	0.45	1403	-1497	-430	4.8

Methyl Orange (OC=0.25)

	x	y	z	B
C(1,M)	23	-210	-2510	4.6
C(2,M)	595	-215	-3207	4.6
C(3,M)	657	-158	-4868	4.6
C(4,M)	146	-95	-5842	4.6
C(5,M)	-426	-90	-5145	4.6
C(6,M)	-488	-147	-3484	4.6
N(1,M)	208	-36	-7562	4.6
N(2,M)	-231	-100	1682	5.4
C(7,M)	-174	-114	-14	5.4
C(8,M)	-687	-128	-985	5.4
C(6,M)	-629	-142	-2651	5.4
C(10,M)	-59	-142	-3356	5.4
C(11,M)	455	-128	-2385	5.4
C(12,M)	397	-114	-719	5.4
N(3,M)	-1	-156	-4992	5.4
C(13,M)	-534	-170	-5962	5.4
C(14,M)	590	-156	-5719	5.4
S(1,M)	-82	-66	-475	4.3
O(1,M)	-237	740	114	4.3
O(2,M)	-506	-629	263	4.3
O(3,M)	511	-258	163	4.3

represented as a superposition of the four structures, I, II, III, and IV of Fig. 3, whose occupancies are 0.25 each.

The successive Fourier maps revealed the locations of the water molecules and cations. The cations are also statistically disordered with the population of 0.25, since there is only one Methyl Orange molecule in the unit cell in spite of four equivalent positions. On the electron density map, the sodium ion was not distinguished from water because of its low population. The location of the sodium cation was considered to be the same as that of the potassium cation, since no significant structural difference was observed between the MONa complex and the MOK complex. On

TABLE 2 (Continued)

α-Cyclodextrin-Methyl Orange Potassium Salt

	OC	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{23}	B_{31}
C(1,G1)	1.00	1549(5)	2429(6)	3555(13)	24(3)	31(4)	100(16)	-13(6)	19(16)	17(12)
C(2,G1)	1.00	1259(5)	2844(7)	5025(16)	15(2)	41(5)	180(21)	-17(6)	22(20)	-10(13)
C(3,G1)	1.00	599(5)	2592(7)	5204(14)	18(3)	45(5)	114(18)	-9(6)	9(18)	-36(12)
C(4,G1)	1.00	258(4)	2772(6)	3665(12)	19(2)	29(4)	92(15)	-2(6)	-2(16)	5(11)
C(5,G1)	1.00	560(5)	2353(8)	2266(14)	17(2)	53(6)	124(19)	-2(7)	50(19)	-2(12)
C(6,G1)	1.00	274(5)	2618(10)	579(14)	18(3)	106(10)	125(20)	3(10)	3(27)	19(13)
O(2,G1)	1.00	1613(3)	2640(5)	6406(10)	18(2)	55(4)	157(14)	-3(5)	-38(15)	-35(9)
O(3,G1)	1.00	324(3)	3030(5)	6520(9)	21(2)	57(4)	97(12)	5(5)	-36(13)	9(9)
O(4,G1)	1.00	-336(3)	2423(4)	3849(8)	14(1)	35(3)	110(11)	-9(4)	14(11)	-8(8)
O(5,G1)	1.00	1193(3)	2631(5)	2163(9)	16(2)	53(4)	114(12)	-3(5)	69(13)	1(8)
O(6,G1)	0.65	530(6)	2192(12)	-618(15)	31(4)	124(12)	86(20)	1(12)	-4(28)	-6(15)
O(6',G1)	0.35	259(13)	3354(18)	184(32)	43(9)	90(17)	188(49)	-6(21)	230(53)	-93(36)
C(1,G2)	1.00	2466(5)	-538(7)	3483(16)	14(2)	35(5)	187(22)	5(6)	20(19)	-4(14)
C(2,G2)	1.00	2632(5)	5(8)	4940(14)	17(3)	46(5)	141(17)	-11(7)	2(22)	7(13)
C(3,G2)	1.00	2177(5)	661(7)	5165(13)	16(2)	37(5)	104(17)	-4(6)	12(16)	19(11)
C(4,G2)	1.00	2079(4)	1130(7)	3600(14)	14(2)	45(5)	125(18)	4(6)	7(19)	-11(12)
C(5,G2)	1.00	1990(6)	572(7)	2127(13)	30(3)	34(5)	82(16)	8(7)	-2(16)	3(13)
C(6,G2)	1.00	2061(7)	1052(8)	568(16)	38(4)	48(6)	158(24)	9(7)	23(22)	-10(17)
O(2,G2)	1.00	2668(3)	-517(5)	6339(10)	21(2)	56(4)	141(14)	10(5)	25(14)	-60(10)
O(3,G2)	1.00	2348(3)	1214(5)	6404(10)	24(2)	50(4)	110(12)	-3(5)	-19(13)	-25(9)
O(4,G2)	1.00	1534(3)	1585(4)	3827(10)	17(2)	38(3)	131(13)	-5(4)	24(12)	-3(8)
O(5,G2)	1.00	2443(3)	-57(5)	2089(8)	20(2)	40(3)	116(11)	2(4)	20(13)	34(8)
O(6,G2)	0.70	2007(9)	568(8)	693(16)	79(7)	48(7)	128(22)	16(12)	5(21)	-3(22)
O(6',G2)	0.30	2566(21)	1318(21)	15(66)	68(15)	52(17)	469(113)	-58(28)	144(83)	17(77)
C(1,G3)	1.00	844(5)	-2932(7)	3576(17)	14(2)	36(5)	206(24)	-6(6)	1(21)	9(14)
C(2,G3)	1.00	1266(5)	-2872(7)	5042(16)	18(3)	37(5)	180(22)	-1(6)	26(20)	-3(14)
C(3,G3)	1.00	1498(5)	-2008(7)	5199(13)	17(3)	47(5)	99(18)	-4(6)	11(18)	-1(11)
C(4,G3)	1.00	1791(5)	-1711(7)	3610(13)	17(2)	40(5)	109(17)	3(6)	29(17)	13(12)
C(5,G3)	1.00	1351(5)	-1841(8)	2189(14)	21(3)	50(6)	95(17)	-9(7)	-13(18)	2(12)
C(6,G3)	1.00	1677(6)	-1665(10)	538(14)	29(4)	85(9)	101(20)	-16(10)	16(23)	40(14)
O(2,G3)	1.00	945(4)	-3161(6)	6411(11)	23(2)	68(5)	176(16)	-10(5)	86(17)	-7(11)
O(3,G3)	1.00	1936(3)	-1979(5)	6432(9)	19(2)	61(4)	113(13)	0(5)	34(14)	-7(9)
O(4,G3)	1.00	1894(3)	-867(4)	3831(9)	13(1)	37(3)	105(11)	2(4)	-2(11)	8(8)
O(5,G3)	1.00	1159(3)	-2675(5)	2152(10)	18(2)	51(4)	149(14)	-9(5)	-43(14)	35(9)
O(6,G3)	0.55	1307(7)	-1776(14)	-642(19)	28(4)	140(16)	116(28)	-53(15)	59(38)	-13(19)
O(6',G3)	0.45	2067(11)	-2101(12)	74(30)	51(8)	47(10)	263(46)	-4(14)	-50(40)	142(35)
K	0.25	1747(9)	4846(8)	754(15)	30(3)	56(6)	193(22)	-13(8)	45(21)	-15(15)
O(W1)	1.00	3300(5)	8358(8)	612(12)	52(4)	101(7)	187(19)	67(9)	51(21)	60(15)
O(W2)	1.00	3786(9)	1225(9)	599(17)	116(8)	119(10)	270(30)	-105(16)	-4(30)	-60(28)
O(W3)	1.00	4293(11)	9785(14)	3383(33)	124(10)	160(16)	1040(91)	7(22)	245(79)	222(60)
O(W4)	1.00	669(11)	4927(11)	2998(27)	148(11)	89(9)	808(66)	11(20)	-43(60)	16(52)
O(W5)	0.75	1633(12)	4884(18)	902(31)	102(11)	173(19)	590(68)	11(27)	92(83)	-32(55)
O(W6)	0.25	0(-)	5000(-)	-137(94)	109(28)	297(71)	909(237)	219(80)	0(-)	0(-)

Hydrogen Atoms

	OC	x	y	z	B
H(1,G1)	1.00	2019	2589	3309	3.8
H(2,G1)	1.00	1267	3532	4937	3.9
H(3,G1)	1.00	555	1941	5508	3.1
H(4,G1)	1.00	260	3441	3398	3.3
H(5,G1)	1.00	523	1671	2522	4.0
H(61,G1)	0.65	357	3280	417	5.1
H(62,G1)	0.65	-223	2504	584	5.1
H(61',G1)	0.35	642	2293	-413	5.1
H(62',G1)	0.35	-195	2387	467	5.1
H(1,G2)	1.00	2797	-1056	3437	3.8
H(2,G2)	1.00	3076	297	4781	4.0
H(3,G2)	1.00	1765	361	5601	3.2
H(4,G2)	1.00	2421	1200	4570	3.2
H(5,G2)	1.00	1538	271	2231	3.9
H(61,G2)	0.70	2533	1300	476	5.1
H(62,G2)	0.70	1738	1565	474	5.1
H(61',G2)	0.30	1851	755	-468	5.1
H(62',G2)	0.30	1773	1605	537	5.1
H(1,G3)	1.00	658	-3563	3557	4.0
H(2,G3)	1.00	1664	-3296	4872	4.5
H(3,G3)	1.00	1128	-1604	5601	3.5
H(4,G3)	1.00	2235	-1992	3359	3.4
H(5,G3)	1.00	930	-1493	2422	3.8
H(61,G3)	0.55	2074	-2051	403	5.2
H(62,G3)	0.55	1835	-1002	540	5.2
H(61',G3)	0.45	1881	-1025	596	5.2
H(62',G3)	0.45	1360	-1584	-429	5.2

Methyl Orange (OC=0.25)

	x	y	z	B
C(1,M)	-6	-234	-254	6.7
C(2,M)	573	-180	-3194	6.7
C(3,M)	648	-116	-4851	6.7
C(4,M)	143	-105	-5860	6.7
C(5,M)	-436	-158	-5203	6.7
C(6,M)	-511	-223	-3546	6.7
N(1,M)	217	-38	-7576	6.7
N(2,M)	-234	-30	1728	7.4
C(7,M)	-172	-57	33	7.4
C(8,M)	-683	-123	-944	7.4
C(9,M)	-621	-149	-2609	7.4
C(10,M)	-48	-111	-3306	7.4
C(11,M)	463	-45	-2328	7.4
C(12,M)	401	-19	-663	7.4
N(3,M)	14	-137	-4940	7.4
C(13,M)	-517	-212	-5916	7.4
C(14,M)	608	-89	-5659	7.4
S(1,M)	-88	-69	-406	6.0
O(1,M)	-223	725	274	6.0
O(2,M)	-513	-638	313	6.0
O(3,M)	508	-293	161	6.0

the difference-Fourier map, the residual electron density was observed near the position of the cation. We considered it to be a water molecule (O(W5)) which occupies the position with the occupancy of 0.75 when the cation is absent. The O(6) atoms in α-CDx were found to be disordered. The occupancies were estimated from the electron density map, but they were not refined.

At this stage, the positions, orientations, and thermal parameters of the SO_3^-, C_6H_4–N, and N–C_6H_4–N-$(CH_3)_2$ groups in Methyl Orange were refined by the rigid-body least-squares method. The bond distances and angles were those from Hanson.[10] In the successive block-diagonal least-squares refinement, the positional and thermal parameters of the Methyl Orange anion were fixed, since the absurd bond lengths of 1.2—1.7 Å were found in benzene rings when the atomic parameters of Methyl Orange anion were allowed to move. Hydrogen atoms can not be found on the difference-Fourier map, but the positions of the

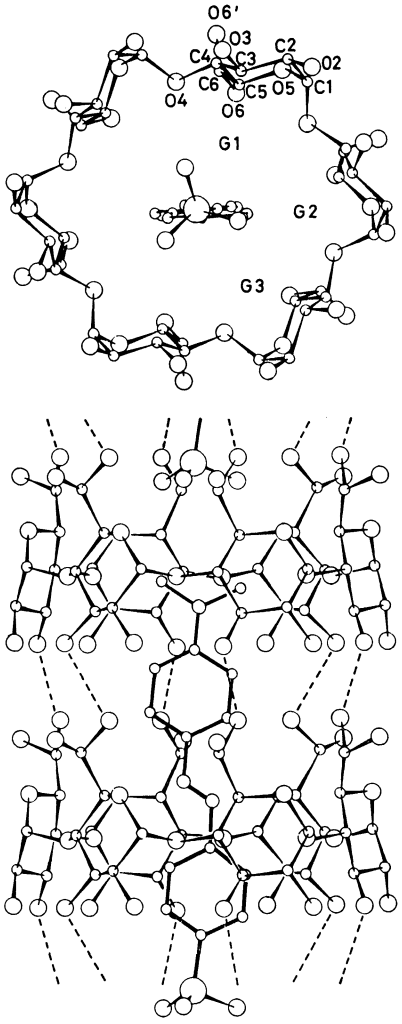

Fig. 4. The structure and numbering scheme of the complex. Dashed lines indicate O(3)···O(6) contacts.

hydrogen atoms attached to the carbon atoms in α-CDx were calculated and included in the structure factor calculation with isotropic thermal factors equal to those of the carbon atoms to which the hydrogen atoms are bonded. The final R-values were 0.11 for the MONa complex and 0.10 for the MOK complex. The quantity minimized was $\Sigma w(|F_o|-|F_c|)^2$ with $w=1.0$ for all the reflections used. The atomic scattering factors were taken from "International Tables for X-Ray Crystallography."[11] The atomic parameters are listed in Table 2, while the observed and calculated structure factors are given in Table 3.*

Description and Discussion of the Structure

The structure of the complex is shown in Fig. 4. Each glucose residue has the Cl chair conformation which is commonly found in α-CDx complexes. The α-CDx molecule is nearly hexagonal and has a two-fold symmetry axis. The α-CDx rings are stacked along the c axis with six hydrogen bonds which connect the O(3) with the O(6) of the adjacent α-CDx molecule, forming channels where Methyl Orange anions are located. The bond distances, angles, and conformation angles are listed in Table 4, the geometrical data for the α-CDx ring are given in Table 6, and the intermolecular distances less than 3.0 Å are shown in Table 7.

Bond Distances and Angles. No significant difference in bond distances and angles is observed between the MONa complex and the MOK complex. The C(1)–O(4*)–C(4*) angles of 117—121° are commonly observed values in α-CDx complexes. Similar values have been also observed in 1,4-linked disaccharides.[12–14]

In both MONa and MOK complexes, abnormally short distances are observed in the disordered C(6)–O(6) bonds. The effects of the thermal motion on the C(6)–O(6) and C(6)–O(6′) bonds were estimated according to Busing and Levy,[15] as is shown in Table 5. The shortening of C–O bonds may be ascribed to the riding motion, since the framework of the α-CDx ring is rigid. The corrected distances, however, are still too short, indicating that the correction for the riding motion is not strictly applicable in this case. The O(6) and O(6′) atoms are bonded to the C(6) atom, whose thermal motion is relatively large. The lower and upper limits for the corrected distances indicate that the effect of thermal motion is remarkably large. The normal C–O distance is found near the midst of the two limits or rather near the upper limit. Kim and Rosenstein[16] have found a similar phenomenon on the disordered C–O bond in α-L-sorbose; the C–O distances are 1.312 and 1.244 Å, and the C–C–O angles are 114.7 and 116.0°. They explained the shortening of the C–O bonds as being due to (1) the statistical overlap of the electron density of oxygen atoms with the hydrogen atoms attached to the carbon atom in the two disordered positions, and (2) a correlation of thermal displacements between C(6) and O(6), O(6)′ which has an effect similar to that of the anti-parallel thermal motion.

Conformation of α-Cyclodextrin. The glucose residues are in the Cl chair conformation and are α-1,4-linked. The disordered primary hydroxyl groups take two orientations: the C(6)–O(6) and C(6)-O(6′) bonds show *gauche-trans* and *gauche-gauche* conformations respectively. A similar disorder has been observed in the 1-propanol complex[7] and the *p*-iodoaniline complex.[8]

The macro-cyclic conformation of α-CDx is described by the conformation angles involving C(1)–O(4*)–C(4*) linkages: C(2)–C(1)–O(4*)–C(4*), O(5)–C(1)–O(4*)–C(4*)–C(1)–O(4*)–C(4*)–C(3*), and C(1)–O(4*)–C(4*)–C(5*). These angles in the Methyl Orange complexes are similar to those in the *p*-iodoaniline complex,[8] but a significant difference is observed in the water complex.[5] The two glucose residues in the water complex are inclined towards the inside of the cavity, thus reducing the empty volume and forming a hydrogen bond with water in it.

The α-CDx ring is distorted from the regular hexago-

* Table 3 is kept at the office of the Chemical Society of Japan. (Document No. 7619)

TABLE 4. BOND DISTANCES(l/Å), ANGLES(ϕ/°), AND CONFORMATION ANGLES(ϕ/°)
An asterisk(*) indicates the atom in the adjacent glucose residue.

α-Cyclodextrin-Methyl Orange Sodium Salt Complex

	G1	G2	G3	AVERAGE
C(1)-C(2)	1.475(26)	1.504(26)	1.534(27)	1.504
C(1)-O(5)	1.465(22)	1.435(22)	1.448(22)	1.449
C(1)-O(4*)	1.397(22)	1.447(22)	1.395(22)	1.413
C(2)-C(3)	1.499(24)	1.581(24)	1.528(26)	1.536
C(2)-O(2)	1.420(21)	1.445(22)	1.345(25)	1.403
C(3)-C(4)	1.529(23)	1.493(24)	1.575(23)	1.532
C(3)-O(3)	1.462(20)	1.422(20)	1.440(20)	1.441
C(4)-C(5)	1.529(25)	1.550(24)	1.499(24)	1.526
C(4)-O(4)	1.427(19)	1.355(20)	1.460(20)	1.414
C(5)-C(6)	1.563(28)	1.542(27)	1.582(27)	1.562
C(5)-O(5)	1.455(22)	1.417(21)	1.477(21)	1.450
C(6)-O(6)	1.297(29)	1.302(34)	1.290(36)	1.296
C(6)-O(6')	1.156(50)	1.233(54)	1.280(44)	1.223

	G1	G2	G3	AVERAGE
C(2)-C(1)-O(5)	108.3(1.5)	108.6(1.5)	109.4(1.5)	108.8
C(2)-C(1)-O(4*)	110.3(1.5)	105.2(1.4)	109.1(1.5)	108.2
O(5)-C(1)-O(4*)	111.0(1.4)	107.6(1.4)	111.3(1.4)	110.0
C(1)-C(2)-C(3)	111.1(1.5)	110.2(1.4)	108.0(1.5)	109.8
C(1)-C(2)-O(2)	110.2(1.4)	108.6(1.4)	106.9(1.6)	108.6
C(3)-C(2)-O(2)	109.3(1.4)	107.4(1.4)	114.4(1.6)	110.4
C(2)-C(3)-C(4)	110.9(1.3)	110.3(1.4)	109.8(1.4)	110.3
C(2)-C(3)-O(3)	112.3(1.3)	110.1(1.3)	108.7(1.4)	110.4
C(4)-C(3)-O(3)	108.5(1.3)	107.2(1.3)	106.8(1.3)	107.5
C(3)-C(4)-C(5)	109.0(1.4)	112.3(1.4)	110.4(1.3)	110.6
C(3)-C(4)-O(4)	107.8(1.3)	106.2(1.3)	102.9(1.2)	105.6
C(5)-C(4)-O(4)	108.1(1.3)	109.5(1.3)	107.8(1.3)	108.5
C(4)-C(5)-C(6)	109.8(1.5)	112.2(1.5)	108.5(1.4)	110.2
C(4)-C(5)-O(5)	108.3(1.4)	112.3(1.4)	107.5(1.3)	109.4
C(6)-C(5)-O(5)	104.8(1.5)	103.0(1.4)	107.5(1.4)	105.1
C(5)-C(6)-O(6)	108.5(1.8)	110.8(2.0)	104.6(2.0)	108.0
C(5)-C(6)-O(6')	123.1(2.9)	122.1(2.9)	122.9(2.4)	122.7
C(1)-O(5)-C(5)	113.1(1.3)	115.9(1.3)	112.4(1.3)	113.8
C(1)-O(4*)-C(4*)	121.3(1.3)	117.5(1.2)	117.7(1.3)	118.8

	G1	G2	G3	AVERAGE
C(1)-C(2)-C(3)-C(4)	-56.4	-54.6	-55.3	-55.4
C(2)-C(3)-C(4)-C(5)	54.8	47.8	56.6	53.1
C(3)-C(4)-C(5)-O(5)	-56.4	-47.7	-57.7	-53.9
C(4)-C(5)-O(5)-C(1)	62.1	54.8	63.8	60.2
C(5)-O(5)-C(1)-C(2)	-62.6	-61.0	-65.2	-62.9
O(5)-C(1)-C(2)-C(3)	57.9	58.6	59.6	58.7
O(4*)-C(1)-C(2)-O(2)	57.6	61.0	61.2	59.9
O(2)-C(2)-C(3)-O(3)	60.3	69.2	69.3	66.3
O(3)-C(3)-C(4)-O(4)	-64.4	-72.7	-71.0	-69.4
O(4)-C(4)-C(5)-C(6)	72.9	79.1	74.6	75.5
O(5)-C(5)-C(6)-O(6)	66.7	67.6	62.0	65.4
O(5)-C(5)-C(6)-O(6')	-52.9	-51.3	-44.7	-49.6
C(4)-C(5)-C(6)-O(6)	-177.2	-171.4	178.0	-176.9
C(4)-C(5)-C(6)-O(6')	63.2	69.8	71.3	68.1
C(2)-C(1)-O(4*)-C(4*)	-129.2	-134.6	-127.1	-130.3
O(5)-C(1)-O(4*)-C(4*)	110.8	110.7	112.1	111.2
C(1)-O(4*)-C(4*)-C(3*)	127.5	130.8	126.6	128.3
C(1)-O(4*)-C(4*)-C(5*)	-111.0	-112.6	-115.8	-113.1

nal symmetry. In the hexagon composed of O(4) atoms, the diagonal O(4,G3)···O(4,G3)* distance is longer by 0.8 Å than the O(4,G1)···O(4,G1)* distance (Table 6). In the 1-propanol complex, the diagonal O(4)···O(4) distances are 8.35—8.57 Å, indicating a nearly regular hexagon. In Methyl Orange complexes, the planarity of the six O(4) atoms is remarkably good; the deviation from the plane are less than 0.006 Å in the MONa complex and 0.012 Å in the MOK complex. In the other α-CDx complexes, the planarity is also rather good. The maximum deviations are 0.136 Å in the water complex, 0.144 Å in the 1-propanol complex, and 0.132 Å in the *p*-iodoaniline complex.

The α-CDx ring is tapered to the O(6) side. The diagonal distances of the cavity are smaller on the O(6) side than on the O(2), O(3) side (Table 6). Although the diagonal O(6)···O(6)* distances are shorter than the C(5)···C(5)* distances, the C(5)–H groups are oriented to the inside of the cavity and the diagonal H···H* distances are smaller than O(6)···O(6)* distances. This neck in the cavity is important in the geometry of the complex. The "guest" molecule may be included in the cavity to fit the slender part of the molecule to the "neck", as in the complexes with iodine and *p*-iodoaniline.

Geometry of Inclusion. The α-CDx molecules are stacked along the c axis to form endless channels with a head-to-tail arrangement, and the "guest" Methyl Orange anions are arranged in the channel. The azo group and one benzene ring are included

TABLE 4. (Continued)

α-Cyclodextrin-Methyl Orange Potassium Salt Complex

	G1	G2	G3	AVERAGE
C(1)-C(2)	1.538(16)	1.544(16)	1.538(16)	1.540
C(1)-O(5)	1.437(13)	1.399(13)	1.435(14)	1.424
C(1)-O(4*)	1.400(13)	1.406(13)	1.418(13)	1.408
C(2)-C(3)	1.522(16)	1.482(16)	1.508(16)	1.504
C(2)-O(2)	1.427(14)	1.442(14)	1.422(15)	1.430
C(3)-C(4)	1.512(15)	1.523(15)	1.545(15)	1.527
C(3)-O(3)	1.441(14)	1.419(13)	1.410(13)	1.423
C(4)-C(5)	1.506(15)	1.540(16)	1.545(16)	1.530
C(4)-O(4)	1.441(12)	1.426(13)	1.413(13)	1.427
C(5)-C(6)	1.597(18)	1.521(18)	1.574(18)	1.564
C(5)-O(5)	1.473(14)	1.436(13)	1.428(14)	1.446
C(6)-O(6)	1.340(21)	1.317(21)	1.287(23)	1.315
C(6)-O(6')	1.244(31)	1.287(48)	1.184(26)	1.238

	G1	G2	G3	AVERAGE
C(2)-C(1)-O(5)	107.8(0.8)	109.5(0.9)	109.7(0.9)	109.0
C(2)-C(1)-O(4*)	107.4(0.9)	105.8(0.9)	108.5(0.9)	107.2
O(5)-C(1)-O(4*)	110.0(0.8)	110.6(0.9)	110.1(0.9)	110.2
C(1)-C(2)-C(3)	110.9(0.9)	110.8(0.9)	109.5(0.9)	110.4
C(1)-C(2)-O(2)	107.6(0.9)	107.7(0.9)	107.9(0.9)	107.7
C(3)-C(2)-O(2)	112.5(0.9)	111.5(0.9)	114.4(0.9)	112.8
C(2)-C(3)-C(4)	110.0(0.9)	110.8(0.9)	111.3(0.9)	110.7
C(2)-C(3)-O(3)	110.0(0.9)	111.9(0.9)	109.0(0.9)	110.3
C(4)-C(3)-O(3)	109.3(0.9)	109.6(0.9)	108.7(0.9)	109.2
C(3)-C(4)-C(5)	109.9(0.9)	113.4(0.9)	110.1(0.9)	111.1
C(3)-C(4)-O(4)	106.7(0.8)	105.8(0.8)	105.4(0.8)	106.0
C(5)-C(4)-O(4)	107.7(0.8)	107.8(0.9)	109.5(0.8)	108.3
C(4)-C(5)-C(6)	112.0(0.9)	110.9(1.0)	110.6(0.9)	111.2
C(4)-C(5)-O(5)	108.9(0.9)	110.7(0.9)	109.6(0.9)	109.7
C(6)-C(5)-O(5)	103.9(0.9)	106.3(0.9)	106.9(0.9)	105.7
C(5)-C(6)-O(6)	109.8(1.2)	110.8(1.2)	110.3(1.3)	110.3
C(5)-C(6)-O(6')	120.4(1.6)	124.5(2.3)	120.4(1.6)	121.8
C(1)-O(5)-C(5)	113.8(0.8)	114.3(0.8)	113.9(0.8)	114.0
C(1)-O(4*)-C(4*)	118.0(0.8)	118.2(0.8)	118.0(0.8)	118.1

	G1	G2	G3	AVERAGE
C(1)-C(2)-C(3)-C(4)	-55.8	-52.0	-53.8	-53.9
C(2)-C(3)-C(4)-C(5)	56.4	47.0	52.6	52.0
C(3)-C(4)-C(5)-O(5)	-57.9	-47.2	-54.0	-53.0
C(4)-C(5)-O(5)-C(1)	62.5	56.5	61.0	60.0
C(5)-O(5)-C(1)-C(2)	-60.6	-62.2	-62.7	-61.8
O(5)-C(1)-C(2)-C(3)	56.4	59.4	57.2	57.7
O(4*)-C(1)-C(2)-O(2)	61.2	62.6	62.0	61.9
O(2)-C(2)-C(3)-O(3)	63.6	65.6	65.3	64.8
O(3)-C(3)-C(4)-O(4)	-66.6	-71.0	-69.5	-69.0
O(4)-C(4)-C(5)-C(6)	72.1	78.3	72.9	74.3
O(5)-C(5)-C(6)-O(6)	66.6	57.3	60.5	61.5
O(5)-C(5)-C(6)-O(6')	-60.6	-47.9	-51.3	-53.3
C(4)-C(5)-C(6)-O(6)	-176.1	177.7	179.8	-179.5
C(4)-C(5)-C(6)-O(6')	56.6	72.5	67.9	65.7
C(2)-C(1)-O(4*)-C(4*)	-130.5	-132.6	-127.9	-130.3
O(5)-C(1)-O(4*)-C(4*)	112.5	109.2	112.0	111.2
C(1)-O(4*)-C(4*)-C(3*)	126.2	130.2	127.3	127.9
C(1)-O(4*)-C(4*)-C(5*)	-112.3	-111.4	-115.0	-112.9

in the cavity; the azo group is located at the "neck" of the cavity. The dimethylamino and sulfonato groups protrude from the O(6) side and the O(2), O(3) side of the cavity respectively, and they are included in the cavities of the adjacent α-CDx molecules. The sulfonato group is located on the O(6) side of the cavity. In the potassium acetate complex, the acetate anion is located on the plane perpendicular to the c axis at a position similar to that of the sulfonato group. It is important that the ionized groups occupy the same position in both complexes, although the dimensions and shapes of the "guest" molecules are quite different. The sulfonato group may be hydrogen-bonded to the primary hydroxyl groups; the distances between oxygen atoms are 2.72, 2.89, 3.02, 3.11, 3.31, and 3.56 Å in the MONa complex, and 2.66, 3.01, 3.05, 3.08, 3.41, and 3.76 Å in the MOK complex. In the potassium acetate complex, the acetate anion is also hydrogen-bonded to four of the primary hydroxyl groups.

The Methyl Orange anion is almost planar except for the sulfonato group. The distortion of the hexagonal α-CDx ring may be ascribed to the inclusion of the bulky and planar "guest" molecule. A similar distortion has been observed in the *p*-iodoaniline complex.[8] The location of the benzene ring is nearly the same in the Methyl Orange complexes and in the *p*-iodoaniline complex. In both complexes, the longest diagonal O(4)···O(4)* distance is found to be nearly parallel to the benzene plane.

Crystal Structure. The framework of the crystal consists of stacked α-CDx molecules along the c axis.

TABLE 5. CORRECTED BOND DISTANCES, UPPER AND LOWER BOUNDS FOR THE C(6)-O(6) AND C(6)-O(6′) BONDS (l/Å)

	Uncorrected	Corrected for riding motion	Lower bound	Upper bound
(1) MONa complex				
C(6,G1)-O(6,G1)	1.297	1.302	1.297	1.549
C(6,G1)-O(6′,G1)	1.156	1.186	1.159	1.428
C(6,G2)-O(6,G2)	1.302	1.341	1.306	1.632
C(6,G2)-O(6′,G2)	1.233	1.259	1.236	1.503
C(6,G3)-O(6,G3)	1.290	1.294	1.290	1.572
C(6,G3)-O(6′,G3)	1.280	1.287	1.280	1.507
(2) MOK complex				
C(6,G1)-O(6,G1)	1.340	1.359	1.342	1.604
C(6,G1)-O(6′,G1)	1.244	1.261	1.245	1.438
C(6,G2)-O(6,G2)	1.317	1.356	1.322	1.613
C(6,G2)-O(6′,G2)	1.287	1.340	1.297	1.577
C(6,G3)-O(6,G3)	1.287	1.325	1.291	1.601
C(6,G3)-O(6′,G3)	1.184	1.193	1.185	1.439

TABLE 6. GEOMETRICAL DATA FOR THE HEXAGON DESCRIBED BY THE O(4) ATOMS

An asterisk(*) indicates the atom in the opposite glucose residue.

(1) Diagonal distances in the α-CDx ring (l/Å)

i) MONa complex

O(4,G1)-O(4,G1)*	8.08	O(6,G1)-O(6,G1)*	7.86
O(4,G2)-O(4,G2)*	8.56	O(6,G2)-O(6,G2)*	8.86
O(4,G3)-O(4,G3)*	8.82	O(6,G3)-O(6,G3)*	8.21
C(3,G1)-C(3,G1)*	8.94	C(5,G1)-C(5,G1)*	8.06
C(3,G2)-C(3,G2)*	9.71	C(5,G2)-C(5,G2)*	9.01
C(3,G3)-C(3,G3)*	9.27	C(5,G3)-C(5,G3)*	8.49

ii) MOK complex

O(4,G1)-O(4,G1)*	8.06	O(6,G1)-O(6,G1)*	7.55
O(4,G2)-O(4,G2)*	8.54	O(6,G2)-O(6,G2)*	9.06
O(4,G3)-O(4,G3)*	8.84	O(6,G3)-O(6,G3)*	8.20
C(3,G1)-C(3,G1)*	8.88	C(5,G1)-C(5,G1)*	8.08
C(3,G2)-C(3,G2)*	9.86	C(5,G2)-C(5,G2)*	8.99
C(3,G3)-C(3,G3)*	9.33	C(5,G3)-C(5,G3)*	8.48

(2) Least-squares planes through six O(4) atoms and deviations of atoms (l/Å)

i) MONa complex

$0.000X+0.000Y+1.000Z=3.148$

O(4,G1)	−0.002	O(4,G2)	−0.004	O(4,G3)	0.006
O(4,G1)*	−0.002	O(4,G2)*	−0.004	O(4,G3)*	0.006

ii) MOK complex

$0.000X+0.000Y+1.000Z=3.180$

O(4,G1)	0.012	O(4,G2)	−0.008	O(4,G3)	−0.004
O(4,G1)*	0.012	O(4,G2)*	−0.008	O(4,G3)*	−0.004

The weak streaks observed in the oscillation photographs indicate that there is a repetition unit of c' which is twice as long as the c length. The Methyl Orange anion is nearly twice as long as the c length, so the repetition unit in one channel may be c' as is shown in Fig. 3. A structure analysis by taking the unit cell length of c' is possible, but we did not attempt it because

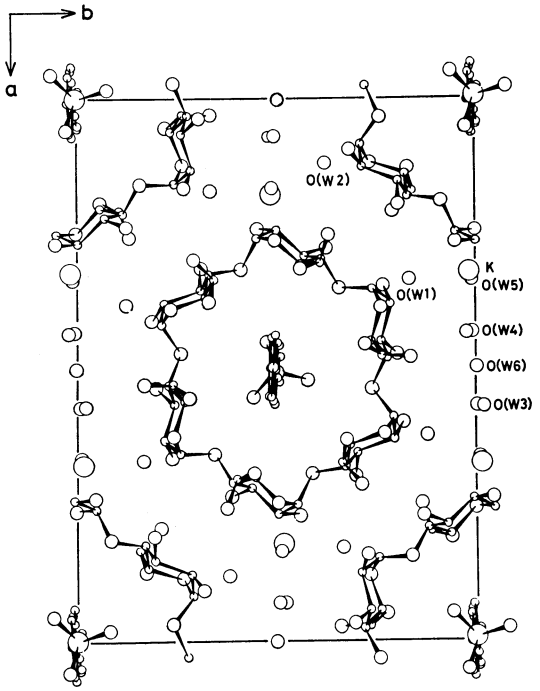

Fig. 5. The projection of the crystal structure of the α-cyclodextrin-Methyl Orange potassium salt complex along the c axis.

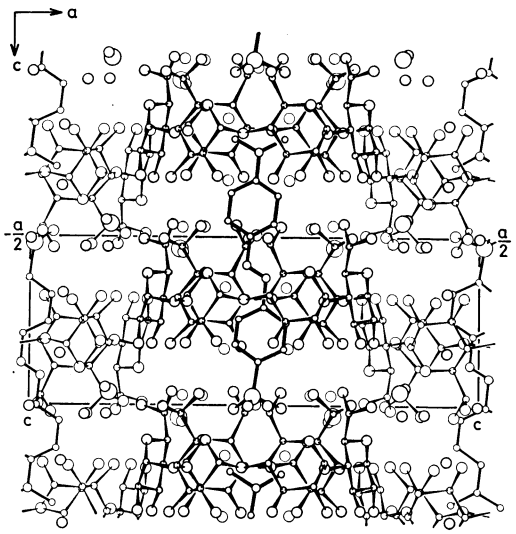

Fig. 6 The projection of the crystal structure of the α-cyclodextrin-Methyl Orange potassium salt complex along the b axis.

the reflections of $(l+1/2)$-th layers were so weak that no intensity measurement was tractable. The weak streaks can be explained if we assume some regularity that appears on the arrangements of the Methyl Orange anion, as is shown in Fig. 3. The disordered arrangements of "guest" molecules are plausible, since the inside of the channel has no contact with other channels. Therefore, the dimensions and shape of the "guest" molecule may be flexible in the channel-type structure, but the location of the ionized group may be very important because of the electrostatic interaction

Table 7. Intermolecular distances (l/Å) less than 3.0 Å

(1) MONa complex								
O(6′,G1)-O(W6)		2.85	O(W1)-O(W5)	(c)	2.85	O(5,G3)-O(W2)	(d)	2.93
O(6′,G2)-O(W2)		2.75	O(6′,G2)-O(6′,G3)	(c)	2.65	Na-O(W1)	(d)	2.51
O(W4)-O(W6)		2.74	Na-O(W2)	(c)	2.89	O(2,G2)-Na	(e)	2.90
O(W4)-O(W5)		2.61	O(5,G2)-Na	(d)	2.86	O(3,G1)-O(W3)	(e)	2.93
O(6′,G3)-O(W1)	(a)	2.86	O(5,G1)-O(W1)	(d)	2.85	O(2,G1)-O(W1)	(e)	2.77
O(3,G1)-O(6,G1)	(b)	2.78	O(6′,G2)-Na	(d)	2.91	O(2,G2)-O(W5)	(e)	2.93
O(3,G2)-O(6,G2)	(b)	2.79	O(W2)-O(W2)	(d)	2.68	O(2,G3)-O(W2)	(e)	2.75
O(3,G3)-O(6,G3)	(b)	2.87						
(2) MOK complex								
O(6′,G1)-O(W6)		2.77	O(6′,G2)-O(6′,G3)	(c)	2.71	O(6′,G2)-K	(d)	2.92
O(6′,G2)-O(W2)		2.74	K-O(W2)	(c)	2.78	K-O(W1)	(d)	2.69
O(W4)-O(W5)		2.75	O(W1)-O(W5)	(c)	2.80	O(2,G2)-O(W5)	(e)	2.84
O(6′,G3)-O(W1)	(a)	2.86	O(5,G2)-K	(d)	2.97	O(2,G1)-O(W1)	(e)	2.75
O(3,G1)-O(6,G1)	(b)	2.78	O(5,G3)-(W2)	(d)	2.91	O(2,G2)-K	(e)	2.80
O(3,G2)-O(6,G2)	(b)	2.74	O(W2)-O(W5)	(d)	2.69	O(2,G3)-O(W2)	(e)	2.74
O(3,G3)-O(6,G3)	(b)	2.82	O(5,G1)-O(W1)	(d)	2.82			

Symmetry code	Symmetry operator	Symmetry code	Symmetry operator
none	x, y, z	c	$1/2-x$, $1/2+y$, $-z$
a	x, $-1+y$, z	d	$1/2-x$, $-1/2+y$, z
b	x, y, $1+z$	e	$1/2-x$, $-1/2+y$, $1-z$

between the anion in the channel and the cation outside the channel. A similar disorder of the "guest" molecule has been found in the 2 : 1 complex of pyromellitic dianhydrate with *trans*-4-methylstilbene.[17]

In the crystal, the hydrogen-bonding contact between primary hydroxyl groups with the *gauche-gauche* conformation is observed between O(6′, G2) and O(6′, G3) ($1/2-x$, $1/2+y$, $-z$). The space outside the channel is filled with water molecules and cations. The water molecules form a hydrogen-bonding network with each other or with hydroxyl groups of α-CDx. O(W1), O(W2), O(W3), and O(W4) are located at positions similar to those in the potassium acetate complex. In Methyl Orange complexes, a relatively small electron density peak was observed at the special position on the electron density map. We considered it that of a water molecule(O(W6)) with an occupancy of 0.25, since it has hydrogen-bonding contacts with water and a hydroxyl group of α-CDx; the distances of O(W6)···O(6′, G1) and O(W6)···O(W4) in the MONa complex are 2.85 and 2.74 Å respectively.

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