  Bull. Chem. Soc. Jpn., 64, 3548—3556 (1991) [Vol. 64, No. 12

Studies on Synthetic Ionophores. IX.[1] X-Ray Crystal Structure Analysis of Potassium, Rubidium, and Cesium Salts of a Synthetic Carboxylic Ionophore

Noriko KASUGA, Seiichi NAKAHAMA, Kazuo YAMAGUCHI,*,†
Yuji OHASHI,†† and Kayako HORI†††
Department of Polymer Chemistry, Faculty of Engineering, Tokyo Institute of Technology, 2-12-1, Ohokayama, Meguro-ku, Tokyo 152
†Department of Materials Science, Faculty of Science, Kanagawa University, Tsuchiya, Hiratsuka, Kanagawa 259-12
††Department of Chemistry, Faculty of Science, Tokyo Institute of Technology, 2-12-1, Ohokayama, Meguro-ku, Tokyo 152
†††Department of Chemistry, Faculty of Science, Ochanomizu University, Otsuka, Bunkyo-ku, Tokyo 112
(Received May 30, 1991)

X-Ray crystal structure data are presented for potassium, rubidium, and cesium salts (**2**, **3**, and **4**) of 2-[[2-[2-[2-[2-[2-[2-[2-(2-hydroxyethoxy)phenoxy]ethoxy]phenoxy]ethoxy]phenoxy]ethoxy]phenoxy]methyl]benzoic acid (**1**). The crystals of the potassium salt (**2**) monohydrate dichloroform solvate ($2 \cdot H_2O \cdot 2CHCl_3$) are triclinic, space group $P\bar{1}$ with two molecules in the unit cell dimensions a=14.517(1), b=16.380(1), c=13.315(1) Å, α=72.313(8)°, β=117.313(8)°, γ=120.853(5)°. R=0.102 for 6351 observed reflections. The crystals of $3 \cdot H_2O \cdot CHCl_3$ are monoclinic, space group $P2_1/a$ with four molecules in the unit cell dimensions a=24.085(6), b=13.068(2), c=13.983(4) Å, β=105.402(32)°. R=0.068 for 5112 observed reflections. The crystals of $4 \cdot H_2O \cdot CHCl_3$ are monoclinic, space group $P2_1/n$ with four molecules in the unit cell dimensions a=24.412(7), b=13.075(2), c=14.077(4) Å, β=106.743(31)°. R=0.071 for 6153 observed reflections. The backbones of **2**, **3**, and **4** form pseudocycles by head-to-tail hydrogen bonding between the terminal carboxylato and hydroxyl groups (O···O distance, 2.672, 2.699, and 2.706 Å, respectively). The conformations about C–C and C–O bonds are gauche and trans respectively, except for two of the C–O bonds which are gauche to make the pseudocyclic backbone bend like the seam of a tennis ball resulting in the formation of cavities fitted for the size of each cation.

Naturally occurring carboxylic ionophores such as monensin and nigericin, which contain a terminal carboxyl group, one or two hydroxyl groups at the other end, and several ether oxygens provided by tetrahydrofuran and tetrahydropyran rings, mediate transport of ions across biological and artificial membranes.[2] They have been studied as antibiotics[3] and have provided an experimental tool for investigating the roles of transmembrane gradients of ions in regulating biological phenomena.[4] Complexation of an ionized ionophore with cations is capable of transporting the cations across membranes and each of the ionophores has a different specificity for various cations.

To understand the complexation properties of the ion carrier, single crystal X-ray structures of various complexes have been analyzed.[5] The conformation of silver salt of monensin in crystal form was first reported in which the monensin anion is held by the head-to-tail hydrogen bondings between the carboxylato group and the two hydroxyl functions of the terminal tetrahydropyran ring to wrap the cation in the cavity.[6] The sodium salts in anhydrous and hydrate crystal forms are nearly identical with one another, and with that of the silver salt complex. However, the structures of the complexes are somewhat different from that of the free acid in terms of the carboxylic acid conformation, the head-to-tail hydrogen bonding, and the conformation of one of the tetrahydrofuran rings.[7,8] Analogous conformations are also found in carboxylic ionophores with the backbones of 21—24 atoms and their complexes.[5,9] The pseudocyclic framework of the ionophores through head-to-tail hydrogen bonding may be called a 'ring' conformation.

However, in the molecular structures of X206 with 28-atoms backbone and its complexes as well as the methyl-substituted analogue (alborixin), the backbone is similar to that of the seam of a tennis ball rather than a ring conformation.[10] Since the backbone of X206 is much longer and more flexible by lack of sterically rigid spiro ring than those of short-chain carboxylic ionophores such as monensin, the pseudocyclic molecule with head-to-tail hydrogen bonding adopts such a 'seam' conformation to form a hydrophobic surface. A ring conformation of monensin and its complexes by head-to-tail hydrogen bonding is rather flat, but enough to form the lipophilic surface of the ionophore molecules. It appears that lipophilicity of the exterior of the complexes with a 'ring or seam' conformation enables these ionophores to transport ions through hydrophobic membranes.

A similar conformation was observed in K^+ complex of a crown ether, dibenzo-30-crown-10.[11] Typical crown ethers with smaller ring sizes have a cavity fitted for coordinated cations in a 'ring' conformation. In this case, however, the cavity size of a 'ring' conformation is too large to be wrapped round potassium ion, but a 'seam' conformation by hinge of the crown ether backbone at two sites form a cavity adjusted for size of

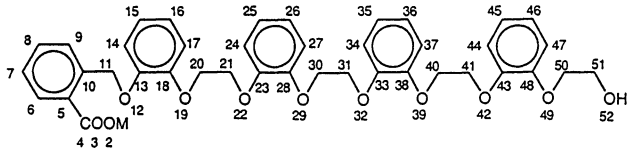
potassium cation resulting in a spherically lipophilic surface of the potassium complex.

We have synthesized a series of linear polyether compounds containing a carboxyl and a hydroxyl groups at one and the other ends as analogues to naturally occurring carboxylic ionophores. Transport of alkali and alkaline earth metal ions mediated by these synthetic ionophores through organic liquid membranes were investigated in terms of effect of the ionophore structures on the ion transport ability and selectivity.[1,12] It was found that the presence of the hydroxyl group, the relative position of the carboxyl group, the number of the ether oxygens, and the hydrophobicity influenced the ion transport ability and selectivity. Among the synthetic carboxylic ionophores, 2-[[2-[2-[2-[2-[2-[2-[2-(2-hydroxyethoxy)phenoxy]ethoxy]phenoxy]ethoxy]-phenoxy]ethoxy]phenoxy]methyl]benzoic acid (**1**) exhibited the highest selectivity for K^+ over Na^+.[13] The backbone of **1** consists of 30 atoms and the length is similar to that of a flexible ionophore (X206) rather than a rigid ionophore (monensin). However, no tetrahydrofuran or tetrahydropyran ring contains in the synthetic ionophore, and instead the molecule is composed of repeating units derived from catechol and ethylene glycol, which largely differs from those of natural ionophores. Therefore, conformations about C–C and C–O bonds are freely rotated except for O–C–C–O of catechol ring. Furthermore, since **1** has neither methyl substituent for aromatic or aliphatic carbon nor hydroxyl group in the backbone, the flexibility is probably higher than that of X206. In fact, the ^{1}H NMR spectra of **1** and the sodium salt show that chemically equivalent protons have the identical chemical shifts one another because of a rapid interconversion between many conformers on the NMR time scale.[13] In contrast, the separation of the chemically equivalent proton resonances was observed in the ^{1}H NMR spectra of the potassium salt (**2**),[13] and the assignments of the signals by two-dimensional NMR methods and the analysis of the proton–proton vicinal coupling constants enabled us to estimate the existing conformations in solution with the highly lipophilic exterior of **2** among many accessible conformations.[14]

Our preliminary X-ray analysis of the potassium salt of **1**, **2**, reveals that the backbone has a conformation similar to those of X206 and the salts, and K^+-alborixin.[15] In this paper we describe the structures of the potassium, rubidium, cesium salts (**2**, **3**, **4**) of the

Table 1. Crystal Data, Experimental Conditions, and Refinement Details of **2**, **3**, and **4**

	2	**3**	**4**
Lattice	Triclinic	Monoclinic	Monoclinic
Formula	$C_{40}H_{39}O_{11}K \cdot H_2O \cdot 2CHCl_3$	$C_{40}H_{39}O_{11}Rb \cdot H_2O \cdot CHCl_3$	$C_{40}H_{39}O_{11}Cs \cdot H_2O \cdot CHCl_3$
Mr	991.61	918.54	966.04
Space group	$P\bar{1}$	$P2_1/a$	$P2_1/n$
a/Å	14.517(1)	24.085(6)	24.412(7)
b/Å	16.380(1)	13.068(2)	13.075(2)
c/Å	13.315(1)	13.983(4)	14.077(4)
α/°	72.313(8)	90.0	90.0
β/°	117.313(8)	105.402(32)	106.743(31)
γ/°	120.853(5)	90.0	90.0
V/Å^3	2406.3(4)	4242.9(18)	4302.7(20)
λ/Å	1.54184	0.71073	0.71073
μ/cm^{-1}	28.53(Cu $K\alpha$)	14.94(Mo $K\alpha$)	10.18(Mo $K\alpha$)
Z	2	4	4
F(000)	938	1884.0	1956.01
D_x/g cm^{-3}	1.374	1.437	1.492
Crystal size/mm	0.8×0.3×0.25	0.3×0.3×0.3	0.3×0.3×0.3
2θ range (°) and	42—60	19—29	19—29
reflections for cell parameter	18	20	16
2θ range/°	3—125	6—50	3—50
Index ranges			
h	−20 to 20	−30 to 30	−24 to 24
k	−23 to 23	0 to 16	0 to 15
l	0 to 18	0 to 17	0 to 16
Scan rate/° min^{-1}	4	8	8
Scan width ω/°	1.0+0.15tanθ	1.0+0.35tanθ	1.0+0.35tanθ
Independent reflections	7693	6273	7864
Observed reflections with $\lvert F_o\rvert > 3\sigma(\lvert F_o\rvert)$	6351	5112	6153
Maximum Δ/σ	0.40	0.06	0.01
Maximum $\Delta\rho$/eA^{-3}	0.44	0.53	0.68
R	0.102	0.068	0.071
R_w	0.126	0.077	0.082



1; M=H
2; M=K
3; M=Rb
4; M=Cs

synthetic carboxylic ionophore (**1**) determined by X-ray crystallography. This study will give us very important information on how a host molecule utilizes local conformational changes to rearrange coordination sites for optimum complexation with a guest cation.

Experimental

Synthesis of carboxylic ionophore (**1**) and the potassium salt (**2**) has been previously described.[13,15] The corresponding rubidium and cesium salts (**3** and **4**) were prepared in a similar manner to that for **2**. Colorless parallelepiped crystals of $2 \cdot H_2O \cdot 2CHCl_3$, $3 \cdot H_2O \cdot CHCl_3$, and $4 \cdot H_2O \cdot CHCl_3$ were obtained from chloroform solutions and sealed in a glass capillary with a drop of chloroform. Crystal data, experimental conditions, refinement details of $2 \cdot H_2O \cdot 2CHCl_3$, $3 \cdot H_2O \cdot CHCl_3$, and $4 \cdot H_2O \cdot CHCl_3$ are shown in Table 1. Intensities of $2 \cdot H_2O \cdot 2CHCl_3$ and $4 \cdot H_2O \cdot CHCl_3$ were collected on a Rigaku AFC-4 four-circle diffractometer; graphite monochromater, Cu $K\alpha$ radiation (45 kV, 25 mA, λ=1.54184 Å) and Mo $K\alpha$ radiation (40 kV, 20 mA, λ=0.71073 Å), respectively. Intensities of $3 \cdot H_2O \cdot CHCl_3$ were collected on a Rigaku off centered four-circle diffractometer; graphite monochorometer, Mo $K\alpha$ radiation (50 kV, 150 mA, λ=0.71073 Å). Cell parameters were obtained by least-squares method. Intensities were measured by using 2θ–ω scan technique. Stationary background counts were accumulated for 5 s before and after each scan. Three standard reflections were monitored every 50 reflections. The intensities of $2 \cdot H_2O \cdot 2CHCl_3$ were not changed significantly, but those of $3 \cdot H_2O \cdot 2CHCl_3$ and $4 \cdot H_2O \cdot CHCl_3$ gradually decreased to 90% compared with their initial values. Corrections were made for Lorentz and polarization, while absorption and extinction were ignored.

The structures were solved by the direct method using the program (MULTAN 78)[16] and subsequent difference Fourier calculation. Refinements were performed by block-matrix least-squares with the program SHELX 76[17] (and block-diagonal least-squares with the program HBLS[18] for $2 \cdot H_2O \cdot 2CHCl_3$). One of the two independent chloroform molecules in $2 \cdot H_2O \cdot 2CHCl_3$ revealed highly disordered structure. Several peaks on the difference map were assigned to the Cl atoms with appropriate occupancy factors. The difference maps of $3 \cdot H_2O \cdot CHCl_3$ and $4 \cdot H_2O \cdot CHCl_3$ showed that the Cl atoms of the chloroform molecule were highly dis-

Table 2. Final Atomic Coordinates of $2 \cdot H_2O \cdot 2CHCl_3$ with Their Estimated Standard Deviations for Non-Hydrogen Atoms ($\times 10^4$) and Equivalent Isotropic Thermal Parameters

Atom		x	y	z	B_{eq}[a]	Atom		x	y	z	B_{eq}[a]
K		7316(1)	8612(1)	1574(1)	4.6	C	30	7665(5)	6989(4)	4380(5)	6.8
O	2	6107(3)	9365(2)	−496(3)	5.7	C	31	8109(5)	7893(5)	4882(4)	6.9
O	3	6819(3)	9180(2)	−1535(3)	5.9	O	32	7660(3)	8496(3)	4020(3)	5.9
C	4	6671(4)	9683(3)	−1132(4)	4.7	C	33	8003(4)	9388(4)	4278(4)	5.6
C	5	7211(4)	10744(3)	−1444(4)	4.9	C	34	8799(5)	9733(5)	5331(5)	7.3
C	6	7256(4)	11062(4)	−2530(4)	5.7	C	35	9082(6)	10636(6)	5487(7)	9.7
C	7	7699(5)	12013(4)	−2878(5)	6.8	C	36	8595(7)	11185(5)	4676(7)	9.4
C	8	8152(5)	12675(4)	−2143(6)	7.6	C	37	7788(5)	10836(4)	3593(6)	7.5
C	9	8139(5)	12387(4)	−1051(5)	6.6	C	38	7514(4)	9937(3)	3434(4)	5.2
C	10	7669(4)	11420(3)	−696(4)	5.2	O	39	6759(3)	9598(2)	2373(3)	5.1
C	11	7704(4)	11129(3)	508(4)	4.9	C	40	5558(4)	9299(4)	2110(5)	5.6
O	12	8442(2)	10664(2)	1145(3)	5.0	C	41	5007(4)	8300(4)	2602(5)	5.4
C	13	9618(4)	11232(3)	1425(4)	4.9	C	42	5018(3)	7696(2)	2038(3)	5.5
C	14	10144(5)	12179(4)	1614(5)	6.7	C	43	4680(4)	6751(3)	2442(4)	5.1
C	15	11355(5)	12716(4)	1896(6)	7.3	C	44	4275(5)	6334(4)	3322(5)	6.4
C	16	11981(4)	12278(4)	2010(5)	6.6	C	45	3971(6)	5370(4)	3684(6)	8.0
C	17	11463(4)	11324(4)	1843(5)	5.8	C	46	4070(5)	4822(4)	3169(6)	7.6
C	18	10265(4)	10798(3)	1551(4)	4.4	C	47	4474(4)	5233(3)	2259(5)	6.2
O	19	9670(2)	9850(2)	1355(3)	4.8	C	48	4770(4)	6205(3)	1914(4)	5.3
C	20	10337(4)	9408(3)	1453(4)	5.0	O	49	5182(3)	6689(2)	1050(3)	6.0
C	21	9560(4)	8384(4)	1226(4)	5.3	C	50	5218(5)	6149(3)	412(4)	5.7
O	22	9068(3)	7949(2)	2077(3)	5.2	C	51	5505(5)	6810(4)	−571(5)	6.2
C	23	8485(4)	6973(3)	2186(4)	5.4	O	52	6643(3)	7568(2)	−175(3)	5.8
C	24	8358(5)	6367(4)	1546(5)	6.7	O	101	3883(4)	8047(4)	9292(5)	9.8
C	25	7747(6)	5380(4)	1755(6)	8.3	C	102	4857(6)	1736(5)	3743(5)	7.5
C	26	7281(6)	5023(4)	2564(7)	8.9	Cl	103	5268(3)	2884(2)	3995(2)	12.0
C	27	7377(5)	5621(4)	3185(6)	7.9	Cl	104	4182(3)	911(2)	4664(2)	12.6
C	28	7983(4)	6606(3)	2972(4)	5.5	Cl	105	5986(3)	1566(3)	3905(3)	15.6
O	29	8139(3)	7294(3)	3525(3)	6.3						

a) $B_{eq}=\frac{8}{3}\pi^2\sum_i\sum_j U_{ij}a_i^*a_j^*\boldsymbol{a}_i\cdot\boldsymbol{a}_j$.

ordered All the non-hydrogen atoms except those of the disordered chloroform molecule were refined with anisotropic thermal parameter. Some hydrogen atoms found on difference Fourier maps and the others derived geometrically (C–H 1.08 Å) were refined isotropically. The quantity minimized was $\sum w(|F_o|-|F_c|)^2$ with $w=(\sigma(|F_o|)^2+0.004|F_o|)^{-1}$. Atomic scattering factors were taken from International Tables for X-ray Crystallography.[19] Calculations were carried out on HITAC M-680 computer at the Computer Center of the University of Tokyo.

Table 3. Final Atomic Coordinates of **3**·H_2O·$CHCl_3$ with Their Estimated Standard Deviations for Rb ($\times10^5$) and Non-Hydrogen Atoms ($\times10^4$) and Equivalent Isotropic Thermal Parameters

Atom		x	y	z	B_{eq}[a)]
Rb	1	37291(3)	6733(5)	67686(5)	4.5
O	2	2896(2)	747(3)	4762(4)	6.0
O	3	3339(2)	−463(3)	4113(4)	5.7
C	4	3166(3)	432(5)	4166(5)	4.6
C	5	3285(2)	1183(5)	3426(5)	4.3
C	6	3234(3)	846(6)	2467(5)	5.3
C	7	3310(3)	1496(7)	1733(5)	6.3
C	8	3454(3)	2512(7)	1968(6)	6.5
C	9	3522(3)	2855(6)	2926(6)	5.7
C	10	3434(2)	2209(5)	3662(5)	4.5
C	11	3524(3)	2618(5)	4701(5)	4.9
O	12	4031(2)	2152(3)	5361(3)	4.6
C	13	4566(3)	2454(5)	5277(4)	4.2
C	14	4669(3)	3381(5)	4869(5)	5.3
C	15	5235(3)	3623(5)	4845(6)	6.0
C	16	5677(3)	2969(6)	5224(6)	5.7
C	17	5572(3)	2029(5)	5636(5)	4.8
C	18	5019(3)	1774(4)	5655(4)	4.0
O	19	4874(2)	880(3)	6038(3)	4.4
C	20	5337(3)	178(5)	6429(5)	4.8
C	21	5095(3)	−779(4)	6743(5)	4.5
O	22	4869(2)	−505(3)	7564(3)	4.3
C	23	4721(2)	−1285(4)	8105(4)	3.9
C	24	4805(3)	−2316(5)	7943(5)	4.7
C	25	4657(3)	−3035(5)	8586(6)	5.6
C	26	4429(3)	−2732(5)	9334(5)	5.1
C	27	4333(3)	−1685(5)	9471(5)	4.5
C	28	4473(2)	−974(4)	8861(4)	3.8
O	29	4388(2)	58(3)	8925(3)	4.1
C	30	4138(2)	399(4)	9673(4)	3.9
C	31	4121(3)	1556(4)	9631(5)	4.3
O	32	3716(2)	1861(3)	8728(3)	4.6
C	33	3629(3)	2901(4)	8593(5)	4.4
C	34	3873(3)	3640(5)	9304(5)	5.2
C	35	3756(3)	4647(5)	9083(7)	6.3
C	36	3400(4)	4947(6)	8175(8)	7.3
C	37	3151(3)	4218(5)	7480(7)	6.3
C	38	3262(3)	3200(5)	7683(5)	4.4
O	39	3042(2)	2464(3)	6969(3)	5.1
C	40	2437(3)	2280(5)	6798(6)	6.3
C	41	2315(3)	1657(6)	7613(6)	6.2
O	42	2538(2)	649(3)	7551(4)	5.7
C	43	2584(3)	−17(6)	8321(5)	5.0
C	44	2428(3)	175(7)	9209(6)	6.5
C	45	2513(4)	−571(8)	9923(6)	7.1
C	46	2757(3)	−1475(7)	9803(6)	6.9
C	47	2898(3)	−1698(6)	8930(6)	5.7
C	48	2812(3)	−965(5)	8190(5)	4.9
O	49	2941(2)	−1088(3)	7303(3)	5.1
C	50	3104(3)	−2077(5)	7063(5)	4.8
C	51	3133(3)	−2042(5)	6001(6)	5.4
O	52	3580(2)	−1379(3)	5906(3)	5.4

a) $B_{eq}=\frac{8}{3}\pi^2\sum_i\sum_j U_{ij}a_i^*a_j^*\boldsymbol{a}_i\cdot\boldsymbol{a}_j$.

Table 4. Final Atomic Coordinates of **4**·H_2O·$CHCl_3$ with Their Estimated Standard Deviations for Cs ($\times10^5$) and Non-Hydrogen Atoms ($\times10^4$) and Equivalent Isotropic Thermal Parameters

Atom		x	y	z	B_{eq}[a)]
Cs	1	62964(2)	7416(4)	29961(3)	4.3
O	2	6652(2)	−417(4)	661(4)	5.3
O	3	7133(2)	819(4)	1666(4)	5.1
C	4	6836(3)	486(5)	854(5)	3.8
C	5	6695(3)	1216(5)	−33(5)	4.1
C	6	6746(3)	856(6)	−925(5)	5.2
C	7	6664(4)	1486(7)	−1759(6)	6.4
C	8	6502(4)	2498(6)	−1686(6)	6.1
C	9	6436(3)	2869(6)	−799(6)	5.4
C	10	6537(3)	2234(5)	37(5)	4.0
C	11	6441(3)	2681(6)	977(5)	4.7
O	12	5954(2)	2196(3)	1176(3)	4.1
C	13	5415(2)	2493(4)	603(5)	3.9
C	14	5301(3)	3414(5)	94(6)	4.9
C	15	4736(3)	3645(6)	−446(6)	5.5
C	16	4296(3)	2971(5)	−458(6)	5.0
C	17	4409(3)	2058(5)	58(5)	4.3
C	18	4968(2)	1813(4)	583(4)	3.5
O	19	5122(2)	908(3)	1122(3)	3.9
C	20	4660(3)	208(5)	1086(5)	4.1
C	21	4916(3)	−739(5)	1662(5)	4.7
O	22	5127(2)	−464(3)	2680(3)	3.9
C	23	5287(3)	−1269(4)	3348(4)	3.7
C	24	5215(3)	−2295(4)	3106(6)	4.8
C	25	5365(4)	−3029(6)	3857(6)	5.7
C	26	5587(3)	−2753(5)	4828(6)	5.6
C	27	5671(3)	−1713(5)	5066(5)	4.3
C	28	5522(3)	−985(4)	4324(4)	3.4
O	29	5590(2)	66(3)	4498(3)	3.6
C	30	5843(3)	386(4)	5499(4)	3.6
C	31	5857(3)	1551(5)	5504(5)	3.7
O	32	6295(2)	1857(3)	5074(4)	4.0
C	33	6386(3)	2908(4)	5050(5)	3.7
C	34	6111(3)	3619(5)	5484(6)	5.2
C	35	6234(4)	4648(5)	5404(7)	6.2
C	36	6639(4)	4953(6)	4943(8)	6.9
C	37	6912(4)	4232(5)	4522(7)	5.7
C	38	6784(3)	3219(4)	4576(5)	4.5
O	39	7038(2)	2493(4)	4112(4)	5.3
C	40	7633(3)	2290(6)	4581(7)	6.3
C	41	7688(3)	1600(5)	5477(7)	6.3
O	42	7492(3)	620(3)	5070(4)	5.1
C	43	7422(3)	−118(5)	5741(5)	4.7
C	44	7552(4)	9(7)	6766(5)	6.4
C	45	7443(5)	−793(8)	7341(7)	7.6
C	46	7202(4)	−1702(8)	6931(6)	6.6
C	47	7093(3)	−1839(6)	5912(5)	5.4
C	48	7203(3)	−1046(5)	5333(4)	4.4
O	49	7105(2)	−1118(4)	4301(3)	4.6
C	50	6920(3)	−2102(5)	3854(5)	4.9
C	51	6924(3)	−2020(6)	2774(5)	5.1
O	52	6477(2)	−1355(4)	2263(4)	5.4

a) $B_{eq}=\frac{8}{3}\pi^2\sum_i\sum_j U_{ij}a_i^*a_j^*\boldsymbol{a}_i\cdot\boldsymbol{a}_j$.

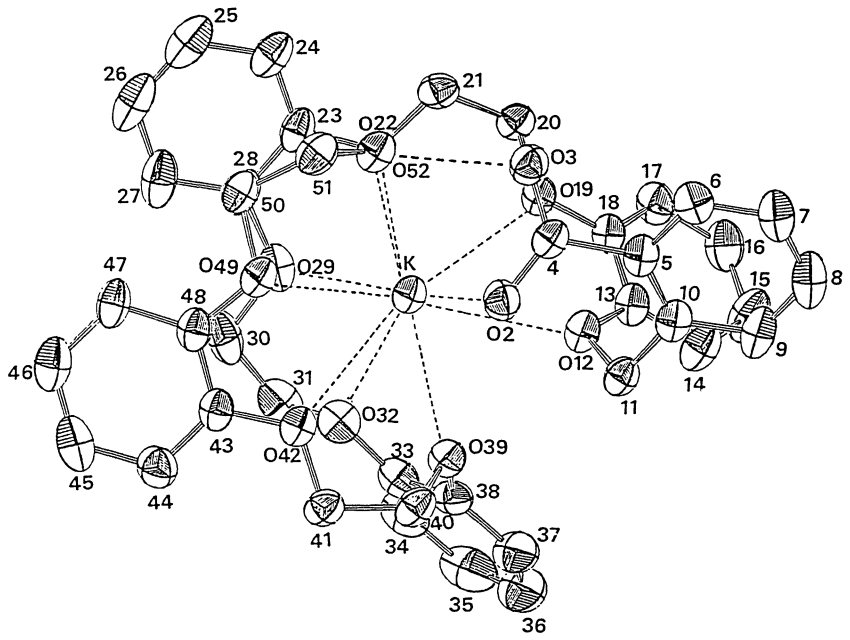


Fig. 1. Molecular structure of **2**. The thermal ellipsoid is 50% probability level. The solid and broken lines indicate coordination and hydrogen bonds, respectively.

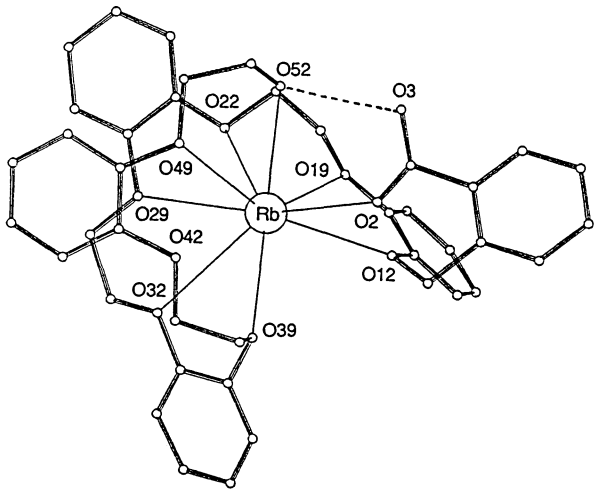


Fig. 2. Molecular structure of **3**. There is no bond between O(42) and Rb.

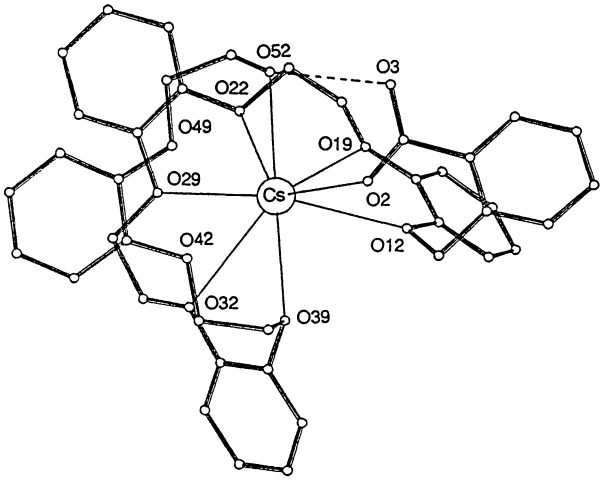


Fig. 3. Molecular structure of **4**. The O(42) has any bond with the Cs ion.

Results and Discussion

Tables 2—4 list the final atomic coordinates and equivalent isotopic thermal parameters of **2**, **3**, and **4**.[20] Molecular structures of **2**, **3**, and **4** are shown in Figs. 1, 2, and 3, respectively. Bond lengths, bond angles, and torsional angles are given in Tables 5, 6, and 7, respectively. They agree well with the usually observed corresponding parameters. In each complex, the intramolecular hydrogen bonding between the carboxylato group and the hydroxyl group at the other end of the molecule produces a pseudocyclic conformation as observed in naturally occurring carboxylic ionophores. The O···O distances are 2.672, 2.699, and 2.706 Å, respectively. As shown in Table 7, the conformations about the aliphatic C–C bonds are gauche with alternate signs through the backbone. Most of the torsion angles about the C–O bonds are close to 180°, whereas both the C(11)–O(12) and O(12)–C(13) bonds and the C(38)–O(39) and O(39)–C(40) bonds have gauche conformations, which play a role of hinges in turning the backbone abruptly. The head-to-tail hydrogen bonding and the torsional angles resulted in the molecular conformation with a thirty-one-membered pseudocycle like the seam of a tennis ball and the ligand wrapped round the potassium ion.

Table 5. Bond Length (Å) in **2**, **3**, and **4**

	2	3	4
O(2)–C(4)	1.261(7)	1.257(9)	1.243(8)
O(3)–C(4)	1.253(7)	1.250(9)	1.264(9)
C(4)–C(5)	1.506(8)	1.508(9)	1.531(9)
C(5)–C(6)	1.401(8)	1.385(10)	1.379(11)
C(5)–C(10)	1.402(8)	1.405(9)	1.397(9)
C(6)–C(7)	1.365(10)	1.380(12)	1.401(12)
C(7)–C(8)	1.375(11)	1.390(13)	1.393(13)
C(8)–C(9)	1.391(10)	1.379(12)	1.392(12)
C(9)–C(10)	1.390(9)	1.389(10)	1.402(10)
C(10)–C(11)	1.512(8)	1.509(10)	1.526(10)
C(11)–O(12)	1.435(7)	1.455(8)	1.445(9)
O(12)–C(13)	1.385(7)	1.383(8)	1.386(8)
C(13)–C(14)	1.378(9)	1.388(10)	1.387(10)
C(13)–C(18)	1.372(7)	1.397(9)	1.400(9)
C(14)–C(15)	1.420(10)	1.408(11)	1.404(12)
C(15)–C(16)	1.355(10)	1.359(11)	1.385(11)
C(16)–C(17)	1.382(9)	1.408(10)	1.383(11)
C(17)–C(18)	1.401(8)	1.381(9)	1.389(9)
C(18)–O(19)	1.376(6)	1.369(7)	1.398(8)
O(19)–C(20)	1.423(7)	1.435(8)	1.442(9)
C(20)–C(21)	1.494(8)	1.494(10)	1.514(11)
C(21)–O(22)	1.425(7)	1.441(8)	1.423(10)
O(22)–C(23)	1.369(7)	1.371(7)	1.391(8)
C(23)–C(24)	1.390(9)	1.389(9)	1.383(10)
C(23)–C(28)	1.362(9)	1.405(8)	1.378(9)
C(24)–C(25)	1.399(11)	1.412(10)	1.397(12)
C(25)–C(26)	1.356(13)	1.362(11)	1.365(12)
C(26)–C(27)	1.381(12)	1.409(10)	1.401(11)
C(27)–C(28)	1.397(10)	1.364(9)	1.383(10)
C(28)–O(29)	1.397(8)	1.370(7)	1.397(8)
O(29)–C(30)	1.428(9)	1.410(7)	1.428(8)
C(30)–C(31)	1.509(11)	1.512(9)	1.523(10)
C(31)–O(32)	1.416(9)	1.431(8)	1.428(8)
O(32)–C(33)	1.379(8)	1.381(8)	1.395(8)
C(33)–C(34)	1.395(10)	1.399(10)	1.388(11)
C(33)–C(38)	1.373(9)	1.398(10)	1.388(10)
C(34)–C(35)	1.373(13)	1.363(12)	1.391(13)
C(35)–C(36)	1.356(14)	1.387(15)	1.388(15)
C(36)–C(37)	1.430(13)	1.379(14)	1.383(15)
C(37)–C(38)	1.373(10)	1.373(11)	1.368(13)
C(38)–O(39)	1.393(7)	1.386(8)	1.395(10)
O(39)–C(40)	1.439(7)	1.433(9)	1.437(11)
C(40)–C(41)	1.494(9)	1.490(12)	1.525(13)
C(41)–O(42)	1.422(7)	1.434(10)	1.429(11)
O(42)–C(43)	1.371(7)	1.366(9)	1.394(10)
C(43)–C(44)	1.386(9)	1.413(12)	1.396(12)
C(43)–C(48)	1.377(8)	1.387(10)	1.382(10)
C(44)–C(45)	1.393(11)	1.371(14)	1.397(14)
C(45)–C(46)	1.375(11)	1.349(14)	1.376(15)
C(46)–C(47)	1.419(10)	1.382(12)	1.393(13)
C(47)–C(48)	1.402(9)	1.385(10)	1.392(11)
C(48)–O(49)	1.378(7)	1.366(8)	1.407(9)
O(49)–C(50)	1.434(8)	1.417(9)	1.446(10)
C(50)–C(51)	1.495(10)	1.506(11)	1.527(11)
C(51)–O(52)	1.430(8)	1.416(9)	1.419(9)

Similar structures with a 29-membered ring through a head-to-tail hydrogen bond are observed in X206, the Na^+ and Ag^+ complexes, and K^+ complex of alborixin.[10] The O···O distances of the hydrogen bonds are 2.91, 2.86, 2.74, and 2.66 Å, respectively. In addition, two other intramolecular hydrogen bonds exist in X206 and the derivatives. These three intramolecular bonds must play a role in the stabilization of the observed structures for the free acid as well as the complexes. In contrast, our synthetic ionophore has a single intramolecular hydrogen bonding. Since a single crystal of **1** has not been obtained so far, the conformation of **1** in the crystal is not known. The free acid may adopt a stable conformation largely different from that of the K^+ complex. X-Ray structure analysis of a crown ether with a thirty-membered ring (dibenzo-30-crown-10) and the complex with KI was reported.[11] Four of the C–C–O–C angles change trans in the free molecule to gauche in the complex. The gauche conformation provides the complex with a structure like the seam of a tennis ball, whereas the free molecule has a rather flat conformation. It appears that the flat conformation of the crown ether is more stable than the 'tennis ball' structure, and coordination of the ether oxygens to the potassium ion in the complex contributes the stabilization of the complex structure.

The overall conformation of **2**, **3**, and **4** is similar to each other as described above, but the cavity size changes by altering the backbone conformation to accommodate the cations with different diameters. Although the difference in bond lengths and angles of **2**, **3**, and **4** is not much as shown in Tables 5 and 6, the torsional angles of the ionophore backbones are significantly different among the three. Compared with the torsional angles about the aliphatic C–C bonds with gauche conformations, the absolute values of **2** are smaller than those of **3** and **4**, except for the case of O(29)–C(30)–C(31)–O(32). Most of dihedral angles about aromatic carbon and oxygen bonds are −6°—+8° except for C(11)–O(12)–C(13)–C(14) and C(37)–C(38)–O(39)–C(40). In the case of C(11)–O(12)–C(13)–C(14), the angle of **2** is larger than those of **3** and **4**. Among aliphatic carbon and oxygen bonds, C(10)–O(11)–C(12)–C(13) and C(38)–C(39)–O(40)–C(41) are gauche. The torsional angle about C(38)–C(39)–O(40)–C(41) of **2** (−98°) is larger than those of **3** and **4**. There is less difference between torsional angles of **3** and **4**. The sum of these conformational changes leads to the different distances between O(12) and O(39), 3.040 Å for **2**, 3.708 Å for **3**, and 4.235 Å for **4**, and to the variety of cavity sizes.

Distances between the ionophore oxygens and the cations are shown in Table 8. With the size of the cations ($K^+ < Rb^+ < Cs^+$), the distance becomes large. The oxygen of terminal hydroxyl group and one of the oxygens of carboxyl group at the other end are close to the cations, but another carboxyl oxygen which has the head-to-tail hydrogen bonding to the terminal hydroxyl group is too distant from the cation to coordinate with them. In addition, two ether oxygens at the hinges have short distances to the cation. Among the two terminal and two internal oxygens of the potassium salt, **2**, the closest oxygen to the potassium is O(39) at the hinge, and then the terminal two oxygens are close and O(12) at the other hinge is furthest. In the case of **3**, the

Table 6. Bond Angles (°) in **2**, **3**, and **4**

	2	**3**	**4**		**2**	**3**	**4**
O(2)–C(4)–O(3)	124.9(5)	125.9(6)	127.0(6)	C(26)–C(27)–C(28)	118.3(7)	120.0(6)	119.9(7)
O(2)–C(4)–C(5)	118.4(5)	117.9(6)	117.8(6)	C(23)–C(28)–C(27)	121.2(6)	119.9(6)	120.7(6)
O(3)–C(4)–C(5)	116.7(5)	116.2(6)	115.1(6)	C(23)–C(28)–O(29)	114.2(5)	115.8(5)	115.7(6)
C(4)–C(5)–C(6)	118.0(5)	118.2(6)	118.1(6)	C(27)–C(28)–O(29)	124.6(6)	124.3(5)	123.5(6)
C(4)–C(5)–C(10)	123.0(6)	123.0(6)	122.6(6)	C(28)–O(29)–C(30)	119.1(5)	117.4(5)	117.2(5)
C(6)–C(5)–C(10)	119.1(5)	118.8(6)	119.3(6)	O(29)–C(30)–C(31)	104.8(6)	107.4(5)	107.5(5)
C(5)–C(6)–C(7)	120.9(6)	121.9(7)	122.2(8)	C(30)–C(31)–O(32)	108.1(6)	108.6(5)	107.3(5)
C(6)–C(7)–C(8)	120.0(7)	119.1(8)	118.2(8)	C(31)–O(32)–C(33)	118.1(5)	116.0(5)	115.6(5)
C(7)–C(8)–C(9)	120.7(7)	119.8(8)	120.4(8)	O(32)–C(33)–C(34)	123.2(6)	124.2(6)	123.2(6)
C(8)–C(9)–C(10)	119.8(6)	121.3(7)	120.5(7)	O(32)–C(33)–C(38)	116.4(6)	115.8(6)	116.1(6)
C(5)–C(10)–C(9)	120.0(6)	119.0(6)	119.4(6)	C(34)–C(33)–C(38)	120.5(6)	119.9(6)	120.7(7)
C(5)–C(10)–C(11)	121.9(5)	121.7(6)	122.7(6)	C(33)–C(34)–C(35)	118.0(8)	118.9(7)	118.0(8)
C(9)–C(10)–C(11)	118.5(5)	119.2(6)	117.8(6)	C(34)–C(35)–C(36)	122.6(9)	121.4(9)	120.9(9)
C(10)–C(11)–O(12)	110.4(5)	110.1(5)	109.9(6)	C(35)–C(36)–C(37)	119.4(9)	119.8(10)	120.1(10)
C(11)–O(12)–C(13)	116.9(4)	118.1(5)	117.4(5)	C(36)–C(37)–C(38)	117.9(7)	120.0(9)	119.3(9)
O(12)–C(13)–C(14)	123.0(5)	123.8(6)	124.0(6)	C(33)–C(38)–C(37)	121.6(6)	120.0(7)	120.8(7)
O(12)–C(13)–C(18)	116.7(5)	115.9(5)	115.9(5)	C(33)–C(38)–O(39)	119.8(5)	119.3(6)	119.6(6)
C(14)–C(13)–C(18)	120.3(5)	120.3(6)	120.2(6)	C(37)–C(38)–O(39)	118.6(6)	120.5(7)	119.6(7)
C(13)–C(14)–C(15)	119.7(6)	119.1(7)	119.0(7)	C(38)–O(39)–C(40)	115.8(4)	114.5(5)	115.9(6)
C(14)–C(15)–C(16)	119.3(7)	120.8(7)	120.5(7)	O(39)–C(40)–C(41)	111.1(5)	111.2(7)	109.0(7)
C(15)–C(16)–C(17)	121.4(7)	120.1(7)	120.4(7)	C(40)–C(41)–O(42)	106.9(5)	107.6(7)	105.0(7)
C(16)–C(17)–C(18)	119.3(6)	119.8(6)	119.7(7)	C(41)–O(42)–C(43)	117.6(5)	119.4(6)	116.2(6)
C(13)–C(18)–C(17)	120.1(5)	119.9(6)	120.2(6)	O(42)–C(43)–C(44)	124.7(5)	126.5(7)	125.6(7)
C(13)–C(18)–O(19)	116.4(5)	115.9(5)	116.1(5)	O(42)–C(43)–C(48)	115.6(5)	114.7(6)	115.8(6)
C(17)–C(18)–O(19)	123.6(5)	124.2(6)	123.6(6)	C(44)–C(43)–C(48)	119.7(6)	118.8(7)	118.6(7)
C(18)–O(19)–C(20)	116.3(4)	116.2(5)	115.6(5)	C(43)–C(44)–C(45)	120.3(7)	119.4(8)	119.1(8)
O(19)–C(20)–C(21)	109.1(5)	108.8(5)	107.6(6)	C(44)–C(45)–C(46)	120.3(7)	121.2(10)	122.3(10)
C(20)–C(21)–O(22)	106.6(5)	106.6(5)	107.8(6)	C(45)–C(46)–C(47)	120.3(7)	120.8(9)	118.4(9)
C(21)–O(22)–C(23)	118.1(5)	117.6(5)	116.1(5)	C(46)–C(47)–C(48)	118.0(6)	119.4(7)	119.6(8)
O(22)–C(23)–C(24)	124.9(6)	124.1(5)	125.2(6)	C(43)–C(48)–C(47)	121.3(6)	120.3(7)	121.9(7)
O(22)–C(23)–C(28)	115.1(5)	115.1(5)	115.2(6)	C(43)–C(48)–O(49)	115.0(5)	114.7(6)	114.7(6)
C(24)–C(23)–C(28)	119.9(6)	120.8(6)	119.6(6)	C(47)–C(48)–O(49)	123.7(5)	125.0(6)	123.4(7)
C(23)–C(24)–C(25)	118.9(7)	118.0(6)	119.5(7)	C(48)–O(49)–C(50)	117.8(5)	117.8(5)	116.6(6)
C(24)–C(25)–C(26)	120.5(8)	121.2(7)	121.2(8)	O(49)–C(50)–C(51)	106.3(5)	107.1(6)	106.2(6)
C(25)–C(26)–C(27)	121.1(9)	120.0(7)	119.0(8)	C(50)–C(51)–O(52)	110.0(6)	110.3(6)	108.9(6)

Table 7. Torsion Angles (°) in **2**, **3**, and **4** Crystals

	2	**3**	**4**
C(10)–C(11)–O(12)–C(13)	+76	+73	+76
C(18)–O(19)–C(20)–C(21)	+179	−176	−177
C(20)–C(21)–O(22)–C(23)	−171	−168	−169
C(28)–O(29)–C(30)–C(31)	+175	+177	+179
C(30)–C(31)–O(32)–C(33)	−177	+177	−178
C(38)–O(39)–C(40)–C(41)	−98	−76	−78
C(40)–C(41)–O(42)–C(43)	+173	+167	+171
C(48)–O(49)–C(50)–C(51)	+171	+172	+172
C(11)–O(12)–C(13)–C(14)	+31	+23	+21
C(17)–C(18)–O(19)–C(20)	−1	−1	−1
C(21)–O(22)–C(23)–C(24)	+2	+4	+5
C(27)–C(28)–O(29)–C(30)	+1	+0	−2
C(31)–O(32)–C(33)–C(34)	+2	−5	−5
C(37)–C(38)–O(39)–C(40)	−76	−74	−73
C(41)–O(42)–C(43)–C(44)	+3	+0	+3
C(47)–C(48)–O(49)–C(50)	+5	+9	+5
O(19)–C(20)–C(21)–O(22)	−48	−66	−68
O(29)–C(30)–C(31)–O(32)	+70	+68	+73
O(39)–C(40)–C(41)–O(42)	−59	−69	−72
O(49)–C(50)–C(51)–O(52)	+57	+65	+70

Table 8. Distance (Å) between Alkali Metal Ion and Oxygen

	2	**3**	**4**
M–O(2)	2.814(4)	2.986(5)	3.144(6)
M–O(3)	3.760(5)	3.876(5)	3.937(6)
M–O(12)	2.890(4)	2.983(4)	3.106(5)
M–O(19)	3.053(4)	3.196(4)	3.296(5)
M–O(22)	2.987(4)	3.085(4)	3.178(5)
M–O(29)	3.038(4)	3.117(4)	3.213(5)
M–O(32)	3.020(4)	3.157(4)	3.270(5)
M–O(39)	2.751(4)	2.923(5)	3.058(6)
M–O(42)	3.156(4)	3.330(5)	3.486(6)
M–O(49)	3.058(5)	3.196(4)	3.330(6)
M–O(52)	2.814(4)	2.923(5)	3.006(6)

ether and terminal hydroxyl oxygens of O(39) and O(52) are closer to the rubidium than O(2) and O(12). The distance from the oxygens to the cesium of **4** increases in the order of O(52)<O(39)<O(12)<O(2). Most of the other oxygens far from the cation are also thought to coordinate with the cations.

The crystal radii (CR) which were calculated and tabulated by Shannon based on the many results of X-ray crystal structure analysis, increase with increasing

coordination number.[21] Values of CR plus van der Waals radius of oxygen (1.4 Å) could be considered as a criterion of the largest coordination distance of oxygen to cation (CD). The CD values of potassium, rubidium, and cesium ions for respective coordination number are illustrated in Table 9. M–O distances of the ionophore complexes in Table 8 are compared with the CD values. The compound, **2**, appears to have ten oxygen donor atoms for the potassium, although the distance between O(42) and K (3.156 Å) is slightly larger than the CD (3.13 Å). Only O(3) (K–O distance 3.760 Å) has no interaction with the potassium as described above. In contrast, the coordination number of **3** is nine: The ninth O(49) is nearly on the coordination sphere of Rb^+, but the distance of 3.330 Å between O(42) and rubidium is larger than the CD of 3.20 Å for ten coordination numbers. Nine oxygen atoms of **4** are also donors for the cesium ion in which the distances between the oxygens and cesium are in the range 3.006 to 3.330 Å. Rubidium and cesium cations of **3** and **4** are nonacoordinated to the oxygens except for O(42) and O(3). These results indicate that the potassium ion of **2** is more stabilized than the rubidium and cesium ions of **3** and **4**, which is consistent with the selectivity of ion transport by **1** as described above.

Compared with a centrosymmetric complex of dibenzo-30-crown-10 with KI that has a 'seam' conformation with ten K–O distances in the range 2.850(6)—2.931(6) Å,[11] the complex structure of **2** as well as **3** and **4** may be a relatively loose arrangement. However, the complex structure of **2** seems to be as stable as that of alborixin-K^+ with another 'seam' conformation in which the eight oxygens from one carboxyl and four hydroxyl groups, and three ether linkages coordinate with the potassium with the distances of 2.70—3.06 Å, while there is no interaction of the other six oxygens with the cation.[10c,d]

The crystal packing of the complex, **2**, is shown in Fig. 4. The molecules of **2** are stacked on (010) plane to generate a layer structure. Two chloroform molecules and one water per one of **2** occupy the interlayer space. One of the two nonequivalent chloroform molecules is highly disordered in a column along the *c*-axis. Crystal structures of **3** and **4** are shown in Figs. 5 and 6. Different from **2**, both of **3** and **4** contain one water and one chloroform molecules which are present between

Table 9. Estimated Largest Coordination Distances (CD) between Oxygen and Cations for Each Coordinaton Number (*n*)

n	CD/Å		
	K^+	Rb^+	Cs^+
8	3.05	3.15	3.28
9	3.09	3.17	3.32
10	3.13	3.20	3.35
11	—	3.23	3.39
12	3.18	3.26	3.42

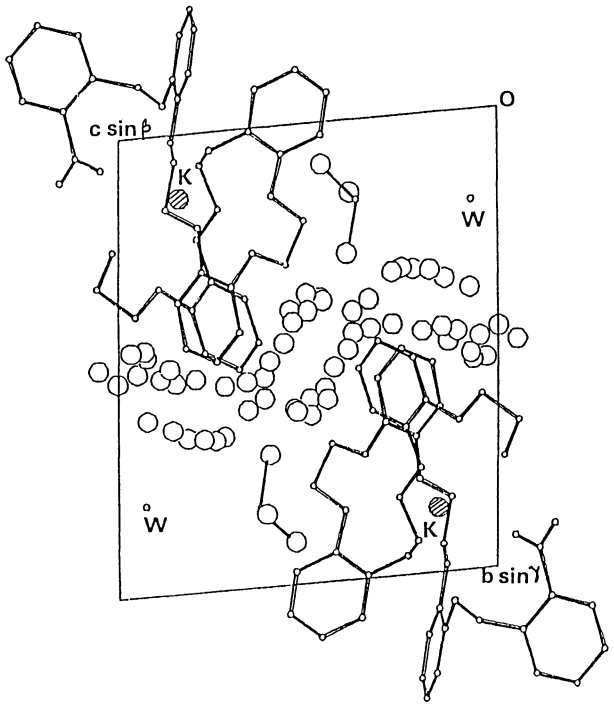


Fig. 4. Crystal structure of $2 \cdot H_2O \cdot 2CHCl_3$ viewed down the *a* axis. The large circles indicate Cl atom of the disordered $CHCl_3$ molecule.

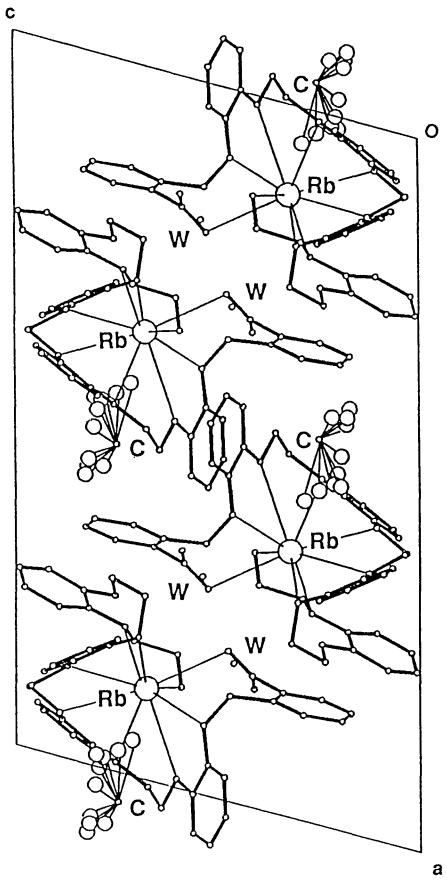


Fig. 5. Crystal structure of $3 \cdot H_2O \cdot CHCl_3$ viewed along the *b* axis.

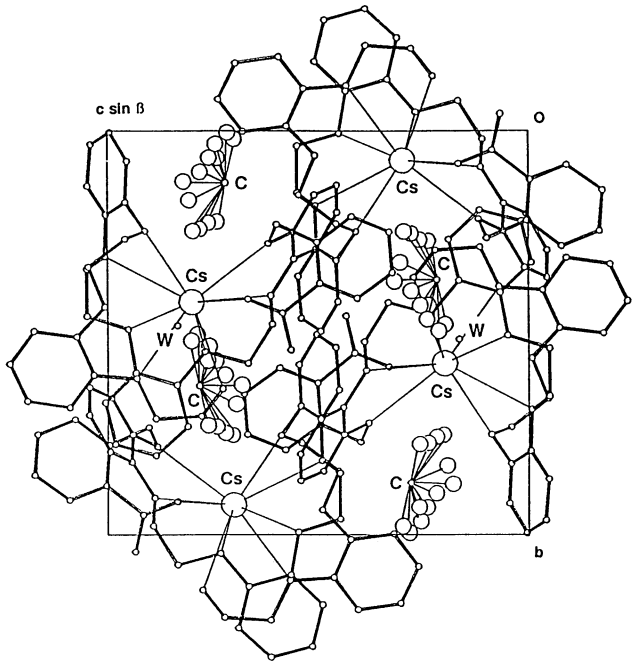


Fig. 6. Crystal structure of $4 \cdot H_2O \cdot CHCl_3$ viewed along the *a* axis. The $CHCl_3$ molecule is highly disordered.

the layer structure formed by the salts. The chloroform molecules are disordered in the interlayer as observed in **2**. These crystal structures with weak interaction between the ionophore molecules of **2**, **3**, and **4** suggest that the alkali metal salts of **1** have stable conformations in chloroform solution similar to those in the crystal.

On the basis of the conformation in the crystal, solution conformations of **2**—**4** by means of NMR spectroscopy are investigated and will be reported in near future.

References

1) Part VIII. K. Yamaguchi, H. Kuboniwa, N. Murakami, A. Hirao, S. Nakahama, and N. Yamazaki, *Bull. Chem. Soc. Jpn.*, **62**, 1097 (1988).

2) G. R. Painter and B. C. Pressman, "Topics in Current Chemistry 101. Host Guest Complex Chemistry II," ed by F. Vogtle, Springer Verlag, Berlin (1982); pp. 83—110, and references cited therein.

3) a) J. W. Westley, *Annu. Rep. Med. Chem.*, **10**, 246 (1975); b) J. W. Westley, *Adv. Appl. Microbiol.*, **22**, 177 (1977).

4) B. C. Pressman, *Annu. Rev. Biochem.*, **45**, 501 (1976).

5) R. Hilgenfelt and W. Saenger, "Topics in Current Chemistry 101. Host Guest Complex Chemistry II," ed by F. Vögtle, Springer Verlag, Berlin (1982); pp. 1—82, and references cited therein.

6) a) A. Agatrap, J. W. Chamberlin, M. Pinkerton, and L. K. Steinrauf, *J. Am. Chem. Soc.*, **89**, 5737 (1967); b) M. Pinkerton and L. K. Steinrauf, *J. Mol. Biol.*, **49**, 533 (1970).

7) W. K. Lutz, F. K. Winkler, and J. D. Dunitz, *Helv. Chim. Acta*, **54**, 1103 (1971).

8) W. L. Duax, G. D. Smith, and P. D. Strong, *J. Am. Chem. Soc.*, **102**, 6725 (1980).

9) a) L. K. Steinrauf, M. Pinkerton, and J. W. Chamberlin, *Biochem. Biophys. Res. Commun.*, **33**, 29 (1968); b) T. Kubota, S. Matsunami, M. Shiro, and H. Koyama, *J. Chem. Soc., Chem. Commun.*, **1968**, 1541; c) M. Shiro and H. Koyama, *J. Chem. Soc. B*, **1970**, 243; d) L. K. Steinrauf, E. W. Czerwinski, and M. Pinkerton, *Biochem. Biophys. Res. Commun.*, **45**, 1279 (1971); e) A. J. Geddes, B. Sheldrick, and W. T. J. Stevenson, *Biochem. Biophys. Res. Commun.*, **60**, 1245 (1974); f) P. Y. Barrans and M. Alleaume, *Acta Crystallogr., Sect. B*, **36**, 936 (1980).

10) a) J. F. Blount and J. W. Westley, *J. Chem. Soc., Chem. Commun.*, **1971**, 927; b) J. F. Blount and J. W. Westley, *ibid.*, **1975**, 533; c) M. Alleaume, B. Busetta, C. Farges, P. Gachon, A. Kergomard, and T. Staron, *ibid.*, **1975**, 411; d) P. V. Roey, W. L. Duax, P. D. Strong, and G. D. Smith, *Isr. J. Chem.*, **24**, 2183 (1984).

11) M. A. Bush and M. R. Truter, *J. Chem. Soc., Perkin Trans. 2*, **1972**, 345.

12) a) H. Kuboniwa, K. Yamaguchi, A. Hirao, S. Nakahama, and N. Yamazaki, *Chem. Lett.*, **1982**, 1937; b) K. Yamaguchi, S. Negi, S. Kozakai, R. Nagano, H. Kuboniwa, A. Hirao, S. Nakahama, and N. Yamazaki, *Bull. Chem. Soc. Jpn.*, **61**, 2047 (1988).

13) H. Kuboniwa, S. Nagami, K. Yamaguchi, A. Hirao, S. Nakahama, and N. Yamazaki, *J. Chem. Soc., Chem. Commun.*, **1985**, 1469.

14) H. Kuboniwa, K. Yamaguchi, A. Hirao, and S. Nakahama, *Magn. Reson. Chem.*, **24**, 961 (1986).

15) H. Kuboniwa, K. Yamaguchi, S. Nakahama, K. Hori, and Y. Ohashi, *Chem. Lett.*, **1988**, 923.

16) P. Main, S. E. Hull, L. Lessinger, G. Germain, J.-P. Declerq, and M. M. Woolfson, MULTAN 78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data. Univs. of York, England and Loivain, Belgium (1978).

17) G. M. Sheldrick, SHELX 76. A Program for Crystal Structure Determination. Univ. of Cambridge (1976).

18) T. Ashida, HBLS V, The Universal Crystallographic Computing System-Osaka, The Computation Center, Osaka University (1973), p. 53.

19) "Intrernational Tables for X-Ray Crystallography, Kynoch Press, Birmingham, England (1974), Vol. IV, p. 71.

20) The positional and thermal parameters of the solvents and hydrogen atoms, the final anisotropic thermal parameters, and $F_o - F_c$ tables are deposited as Document No. 8971 at the Office of the Editor of Bull. Chem. Soc. Jpn.

21) R. D. Shannon, *Acta Crystallogr., Sect. A*, **32**, 751 (1976).