Ring-Enlarged Dibenzo-Crown-6 Ethers.§ Cation Binding and X-Ray Crystal Structure of Dibenzo-22-Crown-6

Mikio OUCHI,* Takashi ARAKI, Tadao HAKUSHI, M. Elizabeth SOBHIA,† Kizakkekoikkal K. CHACKO,*,† Konstantinos SKOBRIDIS,†† and Edwin WEBER*,††

Department of Applied Chemistry, Faculty of Engineering, Himeji Institute of Technology, 2167 Shosha, Himeji, Hyogo 671-22

†Department of Crystallography and Biophysics, University of Madras, Madras 600025, India

††Institut für Organishe Chemie, Technische Universität Bergakademie Freiberg, Leipziger Strasse 29, D-09596 Freiberg/Sa., FR-Germany

(Received February 10, 1993)

The cation binding of dibenzo-20-crown-6 (**2**) and dibenzo-22-crown-6 (**3**) are determined by quantitative solvent extraction study. Compound **3** shows high Tl^+/K^+ and Tl^+/Rb^+ selectivity. The crystal structure of **3** is reported. Crystal data: monoclinic ($P2_1/c$), a=7.328(1), b=17.395(4), c=8.939(1) Å, β=102.78(1)°, Z=2, R=0.049 for 2122 reflections. The macrocycle shows a crystallographic center of symmetry with elliptical arrangement of the heteroatoms stabilized by possible C–H···O dipolar attractions.

In a previous paper, we have reported the synthesis and cation complex formation of "Di- and Triloop Crown Hosts" comprising two or three individual crown macrorings.[1] They involve combinations of benzo-15-crown-5, dibenzo-20-crown-6, and dibenzo-22-crown-6. From the results of cation extraction and solid complex formation, it is shown that these compounds are suitable hosts for the common incorporation of several cations. In the former study, the cation extraction experiments have been performed for measuring the per cent extractabilities defined as per cent picrate extracted into the organic phase. However, a quantitative discussion on the complex formation can not be obtained based on these data. On the contrary, this requires a more quantitative solvent extraction study on the hosts, involving knowledge of the complexation properties of the constituent crown rings included in the present di- and triloop hosts as an essential. For this reason, we wanted to know the complexation behavior of benzo-15-crown-5, dibenzo-20-crown-6 (**2**), and dibenzo-22-crown-6 (**3**), which are equivalent to the constituent crown rings. With regard to benzo-15-crown-5, we have reference to a previous report[2] but not for **2** and **3**, being less symmetrical crowns compared with dibenzo-18-crown-6 (**1**). In a systematic manner, we have determined the cation binding abilities of less symmetrical nonaromatic ($3m+n$)-crown-m ethers.[3] From this point of view, we are also interested to evaluate benzo type crown ethers of low symmetry in respect of their cation complexation.

We report here the cation-binding properties of the ring-enlarged dibenzo-crown compounds **2** and **3** from solvent extraction experiments and discuss the complexation behavior from the extraction equilibrium, including dibenzo-18-crown-6 as a basis for discussion. Also, we were successful in the crystal structure solution of macroring **3** and report these results.

Experimental

Materials. Dibenzo-20-crown-6 (**2**) and dibenzo-22-crown-6 (**3**) were synthesized according to the reported method.[1] Dibenzo-18-crown-6 (**1**), which is commercially available (Aldrich), was a gift from Professor M. Yamamoto of Fukuoka University and it was used without further purification. Alkali metal picrates and heavy metal picrates were synthesized and purified according to the procedures reported previously.[3c,4]

Extraction. The general procedures employed are similar to those described in previous papers.[5,6] Distilled CH_2Cl_2 and demineralized H_2O were saturated with each other before use in order to prevent volume changes of the phases during extraction. Equal volumes (10 mL) of a CH_2Cl_2 solution of the respective dibenzo-crown-6 ether (1—30 mM, 1 M=1 mol dm^{-3}) and an aqueous solution of the metal picrate (fixed at 3.0 mM) were introduced into a stoppered Erlenmeyer flask and shaken for 10 min at 25.0±0.1 °C in a Taiyo M100L incubator. The equilibrated mixture was then allowed to stand for 90 min at that temperature in order to complete phase separation. The organic phase was separated by filtration (Whatman filter paper No. 1PS). The concentration of alkali and heavy metal picrate in the organic phase was determined from absorbance at 375—376 nm in a 1 : 1 mixture of CH_2Cl_2 and acetonitrile as reported.[6,7] In control runs, no detectable amounts of any picrates were extracted into the organic phase in the absence of crown ethers.

According to the extraction equilibrium indicated in the Results and Discussion section, the free crown ether concentration in the organic phase, $[L]_{org}$, was calculated by Eq. 1, where $[L]_i$ is the initial concentration of crown ether dissolved in the organic phase.

$$[L]_{org} = [L]_i - n[M_kL_nA_k]_{org} - [L]_{aq} \quad (1)$$

The distribution of free crown ether between the two phase is expressed as in Eq. 2.

$$L_{org} \overset{K_d}{\rightleftharpoons} L_{aq}$$
$$K_d = [L]_{aq}/[L]_{org} \quad (2)$$

§Polytopic Cation Receptors. IV. Part III of this series, see Ref. 1.

From these independent runs, the distribution coefficients (K_d) of crown ethers between aqueous and organic phase were determined at 25 °C by spectrophotometric analysis. The K_d values were shown to be $\ll 0.0$ and were therefore taken as zero in the calculation. Substitution of $[L]_{aq}$ in Eq. 1 by Eq. 2 leads to Eq. 3, which was actually used to calculate the $[L]_{org}$ values.

$$[L]_{org} = ([L]_i - n[M_kL_nA_k]_{org})/(1 + K_d) \quad (3)$$

X-ray Analysis. (a) Sample Preparation and Data Collection. Crystals of **3** suitable for X-ray analysis were obtained by slow cooling of a solution of **3** in acetone. A colorless crystal of the dimensions of 0.2×0.22×0.35 mm was used and the preliminary unit cell parameters of the complex were determined by photographic methods. Accurate cell parameters were obtained using Enraf–Nonius CAD4 diffractometer equipped with Cu $K\alpha$ radiation (λ=1.5418 Å) by least squares analysis of 2 values of 15 general reflections $20° < 2\theta < 40°$.

Crystal Data: $C_{24}O_6H_{32}$: F_w=497.59, monoclinic, $P2_1/c$, a=7.328(1), b=17.395(4), c=8.939(1) Å, β=102.78 (1)°, V=1111.2(7) Å^3, Z=2, T=296 K, D_c=1.487 g cm^{-3}, μ(Cu$K\alpha$)=1.82 mm^{-1}, $F(000)$=460. Three dimensional data of 2355 reflection were collected and 2122 reflections observed with $I > 2\sigma(I)$, Cu $K\alpha$ radiation, max. 2θ=130, ω–2θ scan, data collected range h=0 to 8, k=0 to 21, l=−10 to 10. No corrections were applied.

(b) Structure Determination and Refinement. The structure was solved by the "Direct Methods" using MULTAN80.[8] It gave most of the non-hydrogen atoms and the remaining non-hydrogen atoms were located from difference Fourier map. The structure was refined with isotropic temperature factors to R of 0.12. Refinement was carried out by full matrix least-squares. All the hydrogen atoms were included in the structure factor calculations in the final stage. The refinement converged at R=0.049, R_w=0.050, $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(|F_o|^2)]^{1/2}$, the quantity minimized was $w[|F_o|^2 - (1/K)|F_c|^2]^2$, where the weight $w = 4|F_o|^2/\sigma|F_c|^2$ and $\sigma|F_o|^2 = \sigma 2(I) + 0.51)2/Lp$, where K is the scale factor and $\sigma(I)$ is the standard deviation in the intensity based on counting statistics. A final difference Fourier showed no relevant peak or trough. All calculations were performed on a VAX-11/730 computer using SDP/VAX.[9] Atomic scattering factors were taken from the literature (Chart 1).[10]

Results and Discussion

Extraction Study. Extraction is a facile and useful method for evaluating the complexing ability of crown ethers with cations.[3,11] In the present study, extractions of aqueous alkali metal picrates (Na^+, K^+, Rb^+, and Cs^+) and heavy metal picrates (Ag^+ and Tl^+) were carried out at 25 °C with dichloromethane solutions of the ring-enlarged benzo-crown ethers **2** and **3**, and the results were compared with those for commercially available dibenzo-18-crown-6 (**1**).

As reported previously,[6] assuming only one extracted species, the overall extraction equilibrium between an aqueous (aq) solution of monovalent metal picrate (MA) and an organic (org) solution of ligand (L) is expressed

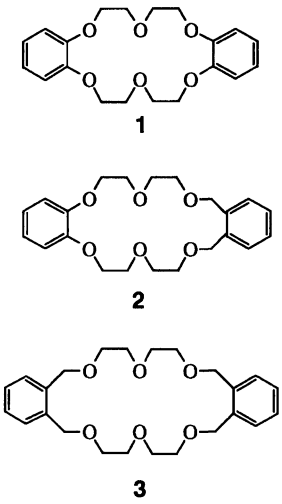

Chart 1.

in the general form of Eq. 4, where the ratio k: n denotes the cation : ligand stoichiometry.

$$kM^+_{aq} + kA^-_{aq} + nL_{org} \rightleftharpoons [M_kL_nA_k]_{org} \quad (4)$$

The equilibrium constant (K_{ex}) is given by Eqs. 5 and 6. Modification of Eq. 5 leads to Eq. 7 with $[L]_{org}$ as a variant.

$$K_{ex} = D_M/k[A^-]^{2k-1}_{aq}[L]^n_{org} \quad (5)$$

$$D_M = k[M_kL_nA_k]_{org}/[M^+]_{aq} \quad (6)$$

$$\log\{D_M/k[A^-]^{2k-1}_{aq}\} = n\log[L]_{org} + \log K_{ex} \quad (7)$$

The extraction equilibrium constant K_{ex} and the complex stoichiometry were determined by using Eq. 7.

Quantitative solvent extraction studies were carried out at a variety of ligand concentrations (1—30 mM) to determine the extraction equilibrium constant K_{ex} and the complex stoichiometry. A set of data obtained for each cation–ligand combination were analyzed assuming the conventional 1 : 1 stoichiometry, dicationic 2 : 1 stoichiometry, and sandwich 1 : 2 stoichiometry. The stoichiometry is verified unequivocally by fitting to the theoretical line for 1 : 1, 2 : 1, and 1 : 2 complexation.

Under the conditions of the present extraction, all cation–ligand combinations fitted for 1 : 1 lines, while the examination of dicationic 2 : 1 lines was not successful. This indicates that dibenzo-20-crown-6 (**2**) and dibenzo-22-crown-6 (**3**) forms 1 : 1 complexes with alkali and heavy metal cations employed. The complex stoichiometry can also be determined by the continuous variation method[7] employed frequently in the homogeneous phase. In the present study, this method was not performed. The K_{ex} values for 1 : 1 cation–ligand complexes thus obtained are given in Table 1. Estimated cavity sizes of **1**—**3** by CPK Molecular Models and cation diameter[12] are shown in Table 2.

We have reported[3] that the unsubstituted less symmetrical ($3m+n$)-crown ethers show lower cation-binding abilities than the symmetrical $3m$-crown-m ether

Table 1. Extraction Equilibrium Constants (K_{ex}) for 1 : 1 Complexations of Dibenzo-Crown-6 Ethers **1**,**2**, and **3** with Alkali- and Heavy Metal Picrates in a Dichloromethane–Water System at 25 °C

	log K_{ex}						Selectivity[a]	
Ligand	Na^+	K^+	Rb^+	Cs^+	Ag^+	Tl^+	Tl^+/K^+	Tl^+/Rb^+
1	2.81[b]	4.84[b]	4.43[b]	4.08[b]	3.74[b]	5.02[b]	1.5	3.9
2	2.32	3.43	3.35	3.23	3.14	4.37	8.7	10.5
3	2.04	2.82	2.96	3.22	3.19	4.41	38.9	28.2

a) Relative cation selectivity determined by K_{ex}. b) Ref. 6.

Table 2. Estimated Cavity Sizes of **1**,**2**, and **3** by CPK Molecular Models and Cation Diameters

	Cavity diameter		Diameter[a]
Crown ether	Å	Cation	Å
1	2.4	Na^+	2.04
2	2.8	K^+	2.76
3	3.7	Rb^+	2.98
		Cs^+	3.40
		Ag^+	2.30
		Tl^+	3.00

a) Ref. 12.

analogs, however, they exhibit significant shift in cation selectivity. The dibenzo-crown-6 ethers **1**—**3** give similar results, and provide some interesting informations, in that they are inconsistent with the data of extractability reported in our previous paper.[1] The ring enlarged less symmetrical dibenzo-20-crown-6 (**2**) and dibenzo-22-crown-6 (**3**) show lower K_{ex} values for all cations employed than the symmetrical dibenzo-18-crown-6 (**1**). Due to the enlarged cavity size, **3** (cavity diameter 3.7 Å) lies selectivity for Cs^+ (cation diameter 3.40 Å), which is in accordance with the size-fit concept.[13] On the other hand, **1** (cavity diameter 2.4 Å) shows selectivity for K^+ (cation diameter 2.76 Å), and **2** (cavity size 2.8 Å) is nonselective among K^+, Rb^+ (cation diameter 2.98 Å), and Cs^+. A comparison between the K_{ex} values of **2** and **3** reveals that they decrease from **2** to **3** for Na^+, K^+, and Rb^+, possibly due to conformational effects. However, it should be noted that the K_{ex} values for Cs^+, Ag^+, and Tl^+ do not change when going from **2** to **3**. This particular behavior is difficult to explain, although the cavity size of **3** should be larger than that of **2**.

A more detailed examination makes evident that the K_{ex} values for Tl^+ are lower in their decrease with increasing methylene chain length than for the alkali metal cations.[14] Thus, for the first time, high Tl^+ selectivity with reference to alkali metal cations has been observed for less-symmetrical dibenzo-crown-6 ethers. Although the cation diameters of K^+, Rb^+, and Tl^+ (cation diameter 3.00 Å) are similar, high Tl^+/K^+ and Tl^+/Rb^+ selectivities were determined for **2** and **3**. This result is rather unexpected[15] considering the simple structure of the crowns.

Table 3. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters of the Non-Hydrogen Atoms for Compound **3** (esd's are in parentheses)

Atom	x	y	z	$B_{eq}/Å^2$
C(1)	1.5159(3)	0.1075(1)	0.3916(2)	4.16(4)
O(2)	1.3712(2)	0.15420(6)	0.3048(1)	3.85(3)
C(3)	1.3369(3)	0.1422(1)	0.1433(2)	3.95(4)
C(4)	1.1375(2)	0.16210(9)	0.0728(2)	3.37(3)
C(5)	1.0963(3)	0.2255(1)	−0.0248(2)	4.18(4)
C(6)	0.9138(3)	0.2445(1)	−0.0920(2)	4.68(5)
C(7)	0.7683(3)	0.2007(1)	−0.0646(2)	4.39(4)
C(8)	0.8074(3)	0.1362(1)	0.0315(2)	3.70(4)
C(9)	0.9895(2)	0.11690(9)	0.1001(2)	3.22(3)
C(10)	1.0324(2)	0.0468(1)	0.2023(2)	3.80(4)
O(11)	0.8641(2)	0.00842(6)	0.2097(1)	4.37(3)
C(12)	0.9004(3)	−0.06374(9)	0.2859(2)	3.87(4)
C(13)	0.7178(3)	−0.1014(1)	0.2907(2)	4.18(4)
O(14)	0.6600(2)	−0.07826(6)	0.4238(l)	4.13(3)
C(15)	0.4931(3)	−0.1139(1)	0.4440(2)	4.30(4)

Table 4. Endocyclic Torsion Angles Involving Non-Hydrogen Atoms of Compound **3** (esd's are in parentheses)

Atoms	Angle/°
C(15*)–C(1)–O(2)–C(3)	−168
C(1)–O(2)–C(3)–C(4)	153
O(2)–C(3)–C(4)–C(9)	−69
C(3)–C(4)–C(9)–C(10)	0
C(4)–C(9)–C(10)–C(11)	−178
C(9)–C(10)–O(11)–C(12)	171
C(10)–O(11)–C(12)–C(13)	180
O(11)–C(12)–C(13)–O(14)	−89
C(12)–C(13)–O(14)–C(15)	−177
C(13)–O(14)–C(15)–C(1*)	160
O(14)–C(15)–C(1*)–O(2*)	−68

X-Ray Structure Study. To know about the structural principles of the ring-enlarged crown-type under discussion is of interest, in particular of macroring **3** that has shown distinct Tl^+/K^+ and Tl^+/Rb^+ selectivities. (cf. Table 1)

Figure 1 shows perspective views (front and side views) of the macrocylce **3**; the crystal packing is depicted in Fig. 2. The final atomic positional parameters

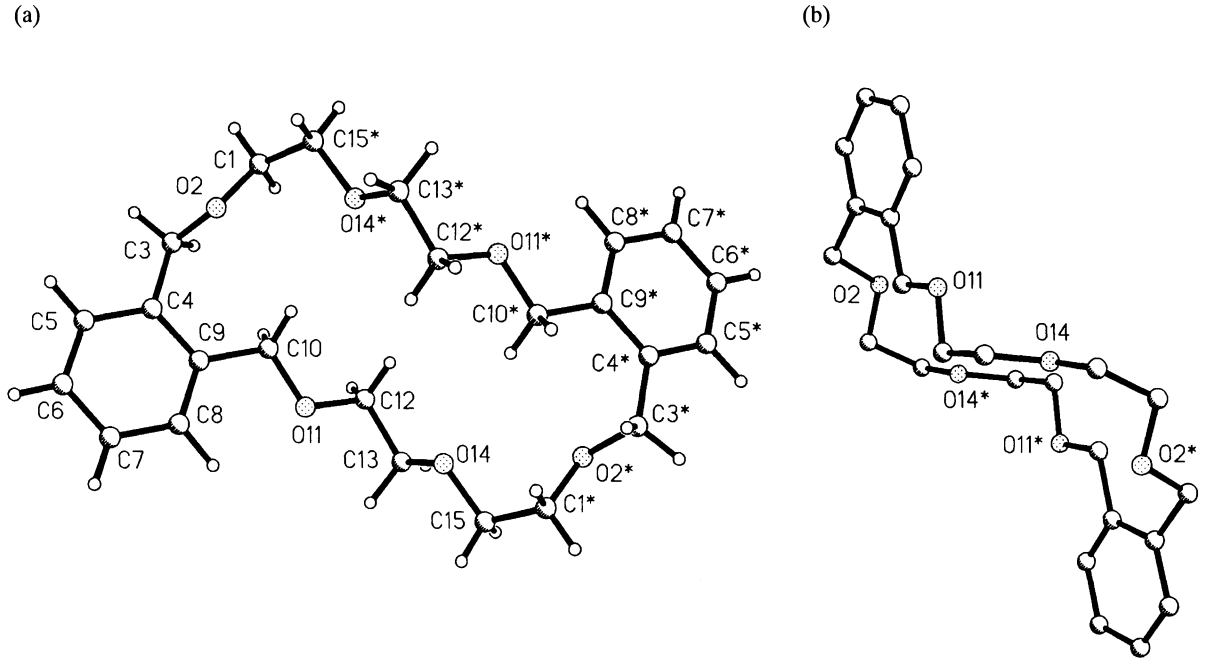

Fig. 1. Perspective views and atom labelling of macroring **3**: (a) top view, (b) side view. O atoms are shaded.

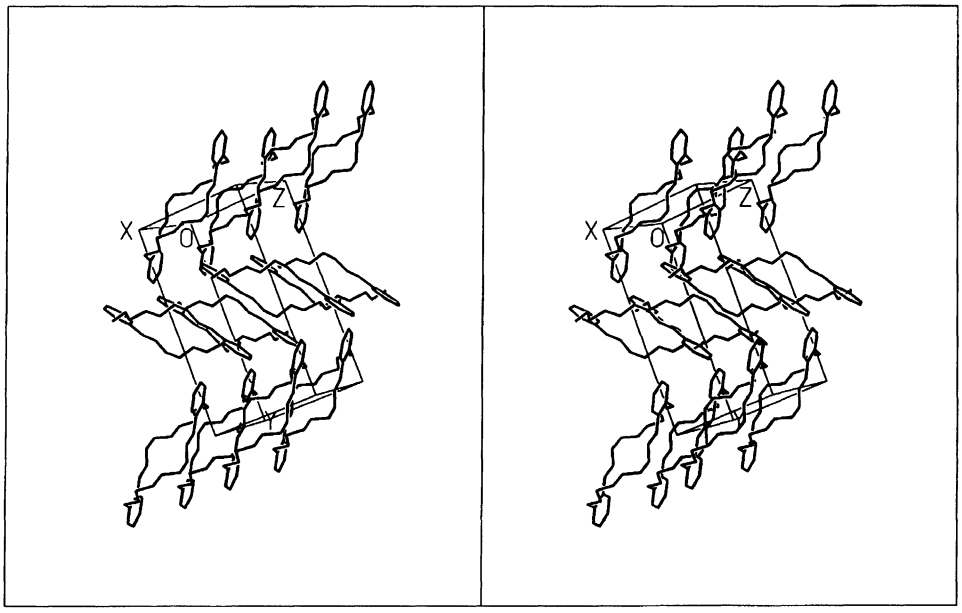

Fig. 2. Stereoscopic packing diagram of **3**. Molecules of **3** are represented as wireframe models.

are given in Table 3; the endocyclic torsion angles are listed in Table 4 and possible C–H···O type interactions are specified in Table 5.[16]

(a) Structure of the Macroring 3. –Bond Parameters. The bond lengths in the benzene moiety range from 1.381(4) to 1.404(2) Å. The mean $C(sp^3)$–$C(sp^3)$ distance [1.499(3) Å] is shorter than the normal value of 1.537 Å,[17] but this follows the trend observed for crown compounds.[18] The mean $C(sp^3)$–O distance is 1.418 Å which is slightly larger than the corresponding distance in the uncomplexed 18-crown-6[19] and lower than the distance in the case of 1,4-dioxane.[20]

It has been suggested that in reported oxanes the C–O–C bond angle is expected to be larger than the O–C–C bond angle.[21] Indeed, in crown ether moieties characterized by a favorable conformation most of the observed O–C–C angles are close to tetrahedral while C–O–C angles are usually 2 to 3° larger.[22] It is also true of the present structure.

Ring Conformation. The macrocyle **3** reveals a chair conformation with a crystallographic centre of symmetry bisecting the O(14)–C(15) and O(14*)–C(15*) bonds (Fig. 1). Individual torsion angles (Table 4) are as usually observed for benzo-crown compounds:[18]

Table 5. Possible C–H···O Type Interactions for Compound **3**[a] (esd's are in parentheses)

Distances/Å			Angle/°
Donor–H	Donor··· Acceptor	H··· Acceptor	Donor–H··· Acceptor
C(10)–H1C(10)^{i}	C(10)··· O(2)	H1C(10)··· O(2)	C(10)–H1C(10)··· O(2)
0.989(16)	3.080(7)	2.568(18)	112(1)
C(1)–H2C(1)^{ii}	C(1)··· O(14)	H2C(1)^{ii}··· O(14)	C(1)–H2C(1)^{ii}··· O(14)
0.958(17)	3.391(2)	2.633(18)	136(1)

a) Symmetrie code: i=x,y,z, ii=$x+1,+y,+z$.

anti (ap) for C–X–C–C (X=O,N), +*gauche* (sc) for O–C–C–O and *syn* (sp) at *ortho*-substituted aryl groups. Starting from the C(1)–O(2) bond, the macroring has the conformation ***aa*g⁻sg⁻aag⁻aagsgaag*aa***. In the current structure, the torsion angles about O(2)–C(3) and C(12)–C(13) are 153 (***a****) and −89 deg. (***g****), respectively, which show distorted *anti* and *gauche* conformations of the macroring. No obvious reasons can be offered to explain the deviation in these torsion angles. Possible intramolecular distances include O(11)···O(14)=3.073 (2) and O(2)···O(14*)=2.816 (5) Å.

Packing Structure. The crystal packing of **3** (Fig. 2) can be described as composed of sheets of different molecular fragments, and the phenylene rings of adjacent molecules displaced along *c* are parallel to and do not overlap each other. The molecules are held together by C–H···O attractions,[24,25] with O(2) and O(14) acting as acceptor sites (Table 5).

Conclusions

Macrocycles such as here featuring the structure of ring-enlarged dibenzo-crown ethers reveal unexpected complexation properties from solvent extraction and membrane electrode studies.[15] In particular they show high selectivity for Tl^+ against K^+ and Rb^+, which is not usual. Hence one may assume that the class of compounds being typical of ring-enlarged benzo- or other arene-fused crowns[26] is a source of ideas for the future design of Tl^+ selective hosts.

In the solid state, the macroring **3** does not have a conformation with optimum position of the oxygen donors for cation complexation. Instead, it shows an oval-shaped centrosymmetric ring structure stabilized by two transannular C–H···O interactions, similar to the centrosymmetric C_i: conformation of uncomplexed 18-crown-6.[22] This structure is characterized by a low internal electrostatic energy, mainly owing to weak repulsion between the unshared electron pairs of the oxygen atoms. However, in the complexes of 18-crown-6 the centrosymmetric D_{3d} structure is the most commonly observed.[22,27] A similar conformation is also likely for the cation complexes of **3**. Nevertheless, this may not primarily account for the high Tl^+/K^+ and Tl^+/Rb^+ selectivities revealed of **3**. Further studies are required to unveil the true facts about the observed selectivity behavior. In order to survey Tl^+ selectivity, studies on complexation thermodynamics of **2** and **3**, and cation binding by less-symmetrical benzo-18 to 20-crown-6 ethers are in progress.

The present work was partially supported by Taki Chemical Co., and a Grant-in-Aid for Scientific Research No. 04750705 from the Ministry of Education, Science and Culture. Thanks are due to the Council of Scientific and Industrial Research, New Delhi, for the award of a Senior Research Fellowship to Ms. Sobhia. E. W. is grateful to the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. M. O. is grateful to Professor Reizo Dohno and Dr. Yoshihisa Inoue of Himeji Institute of Technology for their helpful discussions.

References

1) Part III : E. Weber, K. Skobridis, M. Ouchi, T. Hakushi, and Y. Inoue, *Bull. Chem. Soc. Jpn.*, **63**, 3670 (1990).

2) a) Y. Takeda, *Bull. Chem. Soc. Jpn.*, **56**, 931 (1983); b) Y. Takeda, *Bull. Chem. Soc. Jpn.*, **55**, 2040 (1982); c) H. -J. Buschmann, *Chem. Ber.*, **118**, 2746 (1985); d) R. M. Izatt, R. E. Terry, D. P. Nelson, Y. Chan, D. J. Eatough, J. S. Bradshaw, L. D. Hansen, and J. J. Christensen, *J. Am. Chem. Soc.*, **98**, 7626 (1976).

3) a) M. Ouchi, Y. Inoue, Y. Liu, and T. Hakushi, "Solvent Extraction 1990," ed by T. Sekine, Elsevier, Amsterdam (1992), Part A, p. 363; b) M. Ouchi, Y. Inoue, T. Kanzaki, and T. Hakushi, *J. Org. Chem.*, **49**, 1408 (1984); c) Y. Inoue, M. Ouchi, and T. Hakushi, *Bull. Chem. Soc. Jpn.*, **58**, 525 (1985).

4) K. H. Wong, and H. L. Ng, *J. Coord. Chem.*, **11**, 49 (1981).

5) M. Ouchi, Y. Inoue, K. Wada, S. Iketani, T. Hakushi, and E. Weber, *J. Org. Chem.*, **52**, 2420 (1987).

6) Y. Inoue, Y. Liu, F. Amano, M. Ouchi, A. Tai, and T. Hakushi, *J. Chem. Soc., Dalton Trans.*, **1988**, 2736.

7) A. Sadakane, T. Iwachido, and K. Toei, *Bull. Chem. Soc. Jpn.*, **48**, 60 (1975).

8) P. Main, S. J. Fiske, S. E. Hull, L. Lessinger, G. Germain, J. P. Declercq, and M. M. Woolfson, " MULTAN 80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data," Univ. of York, England and Louvain, Belgium (1980).

9) "Enraf–Nonius Structure Determination Package,"

Enraf–Nonius, Delft, Netherlands (1982).
10) D. T. Cromer and J. T. Waber, "International Tables for X-Ray Crystallography," ed by J. A. Ibers, Kynoch, Birmingham, UK (1974) (distributed by Kluwer, Dordrecht, The Netherlands), Vol. IV.
11) a) Y. Takeda, in "Host Guest Complex Chemistry III," (Topics in Current Chemistry, Vol. 121), ed by F. Vögtle and E. Weber, Springer-Verlag, Berlin–Heidelberg (1984), p. 1; b) K. Gloe, P. Mühl, J. Beger, E. Uhlemann, and L. Beyer, *Wiss. Ber. (Dresden), Akad. Wiss. D. D. R.*, **44**, 83 (1990).
12) R. D. Shannon, *Acta Crystallogr., Sect. A*, **A32**, 751 (1976).
13) For the earliest description of the concept, see: C. J. Pedersen, *J. Am. Chem. Soc.*, **89**, 7017 (1967).
14) We are indebted to Professor T. Shono of Osaka Institute of Technology for his suggestion to discuss Tl^+ selectivity.
15) As a preliminary communication, Tl^+ selective electrode based on less-symmetrical dibenzo-crown-6 were reported. See: Y. Yamashoji, M. Tanaka, S. Nagamune, M. Ouchi, T. Hakushi, and T. Shono, *Anal. Sci.*, **7**, 485 (1991).
16) The lists of intramolecular bond lengths and angles involving the non-hydrogen atoms (Tables 6 and 7), coordinates of the hydrogen atoms (Table 8), bond distances and bond angles involving the hydrogen atoms (Tables 9 and 10), anisotropic vibrational parameters of the non-hydrogen atoms (Table 11) as well as the observed and calculated structure factors are deposited as Document No. 66030 at the Editor of the Office of the Bull. Chem. Soc. Jpn.
17) F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, **1987**, 51.
18) a) R. Hilgenfeld and W. Saenger, *Top. Curr. Chem.*, **101**, 1 (1982); b) R. Panneerselvam, M. E. Sobhia, K. K. Chacko, E. Weber, H. -J. Köhler, and R. Pollex, *J. Inclusion Phenom.*, **13**, 29 (1992).
19) J. O. Dunitz and P. Seiler, *Acta Crystallogr., Sect. B*, **B30**, 2769 (1974).
20) M. David and O. Hassel, *Acta Chem. Scand.*, **26**, 1471 (1968).
21) H. Pickelt and H. L. Strauss, *J. Chem. Phy.*, **53**, 376 (1970).
22) I. Goldberg, in "Crown Ethers and Analogs," ed by S. Patay and Z. Rappoport, Wiley, Chichester (1989), pp. 359 and 399.
23) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca (N. Y.) (1960).
24) F. H. Allen, O. Kennard, and R. Taylor, *Acc. Chem. Res.*, **16**, 146 (1983).
25) G. R. Desiraju, *Acc. Chem. Res.*, **24**, 290 (1991).
26) D. N. Reinhoudt and F. de Jong, in "Progress in Macrocyclic Chemistry," ed by R. M. Izatt and J. J. Christensen, Wiley, New York (1979), Vol. 1, p. 157.
27) E. Weber, in "Synthesis of Macrocycles—The Design of Selective Complexing Agents," (Progress in Macrocyclic Chemistry, Vol. 3), ed by R. M. Izatt and J. J. Christensen, Wiley, New York (1987), p. 337.