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New Applications of Crown Ethers. X.[1] ^{13}C NMR Relaxation Times Study of Cation-Binding Behavior of Monoazacrown Ethers and Bis(monoazacrown ether)s

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^{13}C NMR relaxation times (T_1s) have been determined for monoazacrown ethers (**CA15C5** and **CA18C6**) and bis(monoazacrown ether)s (**BCA15C5, BCA18C6, BOA15C5,** and **BOA18C6**) in the absence and presence of Na$^+$ and K$^+$ ions. For the monoazacrown ethers with heptyl side chain and the bis(monoazacrown ether)s with pentamethylene bridge chain marked changes in T_1 values are observed upon the complexation, and the changes are dependent on the cation and on the structure of the ligands. The complexation with Na$^+$ ion can give a larger effect on the T_1 values for the bis(monoazacrown ether)s of 15- and 18-membered rings, especially on the mobility of the bridging chain carbons, which is indicative of the formation of an intramolecular sandwich complex. On the other hand, the present T_1 study again shows the prominent effect of the oxygen in the bridging chain on the complexation of **BOA15C5** and **BOA18C6**. Small differences in T_1 values obtained between Na$^+$ complexes and K$^+$ complexes of these two bis(crown ether)s suggest that the complexes take an analogous partial structure for the two cations.

Bis(crown ether)s are well-known to bind a cation, which is larger in size than the hole of crown unit, to form an intramolecular sandwich complex, and to show remarkable enhancement of the binding ability and changes of the selectivity in comparison with their monocyclic analogues.[2,3] Such a 'biscrown effect' has been found for many bis(crown ether) compounds both in two-phase system and in homogeneous solution.[4–6] A systematic study showed that the 'biscrown effect' is pronounced in the combination where the ratio of hole size to cation diameter is smaller than 1 in the complexation of bis(benzocrown ether)s with alkali-metal cations in the solution. Bis(benzo-15-crown-5)s can form the intramolecular sandwich complex with K$^+$, Rb$^+$, and Cs$^+$, and bis(benzo-18-crown-6)s act similarly with Rb$^+$ and Cs$^+$. On the other hand, for the systems of bis(benzo-15-crown-5)s-Na$^+$, bis(benzo-18-crown-6)s-Na$^+$, and bis(benzo-18-crown-6)s-K$^+$ only 2:2 (cation: crown unit) complex could be found.[6] For relatively flexible crown ether compounds, however, such a relationship is not so clear. Gokel and co-workers pointed out that N-pivot lariat ethers, a flexible macrocycle, are directed by the cation to envelop and solvate in the geometry most appropriate for the cation and not for the macrocycle.[7,8] Our previous results showed that both bis(monoaza-15-crown-5)s and bis(monoaza-18-crown-6)s can form the intramolecular sandwich complex even with small Na$^+$ ion, and examination of concentration-dependent changes in ^{13}C NMR chemical shift also supported the proposed structure of the complexes.[9] The conclusion is in line with the idea that the "induced fit" concept is more suitable than the "lock and key" concept for understanding the binding behavior of such flexible crown ethers.[9]

^{13}C NMR spin-lattice relaxation time (T_1) determination has been used to study the complexation behavior of many mono(crown ether)s and cryptands, and was shown to provide further insights into the ligand's structural properties, binding strengths, and binding dynamics.[10–13] Especially, this technique offers a convenient method to assess the presence of specific interactions between the bound cation and the different sites of the ligand molecule. In this paper the results of ^{13}C NMR relaxation time determination for monoazacrown ethers, bis(monoazacrown ether)s and their complexes are reported. The experiment was carried out to get detailed information on the

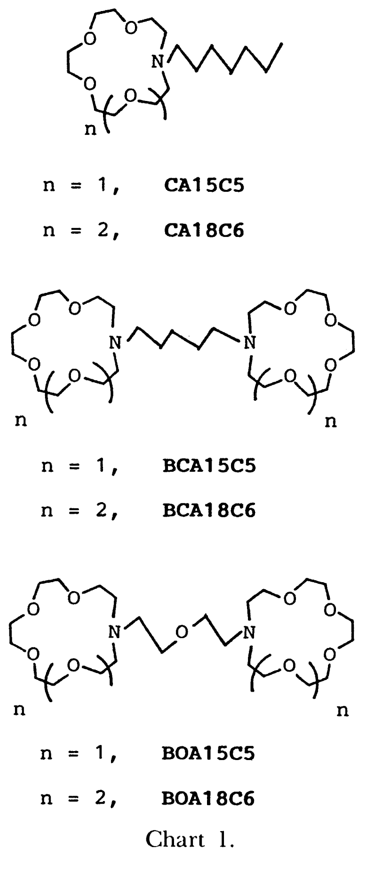

n = 1,　CA15C5
n = 2,　CA18C6
n = 1,　BCA15C5
n = 2,　BCA18C6
n = 1,　BOA15C5
n = 2,　BOA18C6

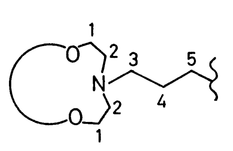
Chart 1.

microstructural interaction in the complexes of bis(monoazacrown ether)s, especially, for the formation of the intramolecular sandwich complex.

Experimental

Material. Monoazacrown ethers and bis(monoazacrown ether)s used here were prepared as previously described.[9,14] They were distilled under vacuum prior to use. Their structures and abbreviated names are shown in Chart 1. Sodium and potassium thiocyanate were purchased (Katayama) and dried in vacuum at least for 48 h before use. All solvent were spectral grade: 99.95% D_2O (Merck) and 99.8% CH_3OH(Kishida).

T_1 Measurements. NMR samples consisted of 0.5 ml of solution in 5-mm o.d. tubes which were sealed under vacuum after degassing by 5 freeze-pump-thaw cycles. All glassware was washed with 0.01 M EDTA solution to remove paramagnetic impurities. Relaxation time experiments were performed in $CH_3OH : D_2O = 90 : 10$ (w/w) solutions 0.4—0.8 M (1 M=1 mol dm^{-3}) in the appropriate ethers. It was reported that no concentration dependence of T_1 was detected under the conditions.[10] Only the carbons 1—5 in Scheme 1 were assigned through the spectra determined under the non-NOE decoupling conditions. The T_1 values for the rest of the side-arm carbons for *N*-heptylmonoazacrown ethers were not determined. For Na$^+$ complexes of **BOA15C5** and **BOA18C6** the bridging chain carbon C-4 shows the same chemical shift with the ring carbon C-1, so that the two carbon atoms give only one T_1 value for Na$^+$-**BOA15C5** and Na$^+$-**BOA18C6** in Tables 1 and 2, respectively, which should be the average values for the two carbons. Since only single decay was observed for the two carbons in the T_1 determination the T_1 values for the two carbons should be close.



Scheme 1.

^{13}C NMR measurements were performed at 22.5 MHz on a Hitachi R-90HS spectrometer equipped with quadrature phase detection system. Relaxation times (T_1s) were measured under proton-noise-decoupling conditions by the inversion-recovery technique. A waiting time (t_w) of at least five times the longest relaxation time was used in each case. Three kinds of pulse sequence were used to determine T_1 for different carbon atoms: for solvent methanol, t_w=100 s, 14 different pulse intervals τ=4—50 s, 10 scans; for monoazacrown ethers, t_w=30 s, 16 different pulse intervals τ=0.1—5 s, 80 scans; for bis(monoazacrown ether)s, t_w=30 s, 16 different pulse intervals τ=0.05—3 s, 120 scans. All spectra were recorded at 35±1 °C, and each run took 6—16 h. T_1 values were determined by a linear least-squares, two-parameter fit of the experimental data directly performed by the spec-

Table 1. ^{13}C NMR Relaxation Times (T_1) for Monoaza-15-crown-5, Bis(monoaza-15-crown-5)s, and Their Cation Complexes in 90%(w/w) Methanol Aqueous Solution[a)]

Crown	Cation	logK_s	C-1	C-2	C-3	C-4	C-5	CH_3
CA15C5	None	—	1.06	1.02	1.40	2.45	1.85	4.47
	Na$^+$	2.76	0.83(22%)	0.89(13%)	1.37(2%)	2.54(−4%)	2.10(−14%)	4.33(3%)
	K$^+$	2.29	0.54(49%)	0.67(34%)	0.75(46%)	2.50(−2%)	1.89(−2%)	3.79(15%)
BCA15C5	None	—	0.77	0.52	0.46	0.56	0.66	—
	Na$^+$	2.82	0.47(39%)	0.46(12%)	0.45(2%)	0.45(20%)	0.45(32%)	—
	K$^+$	2.69	0.53(31%)	0.50(4%)	0.48(−4%)	0.46(18%)	0.67(−2%)	—
BOA15C5	None	—	0.82	0.66	0.62	0.73	—	—
	Na$^+$	3.63	0.62(24%)	0.54(18%)	0.50(19%)	0.62(14%)	—	—
	K$^+$	3.70	0.61(26%)	0.55(17%)	0.53(15%)	0.64(11%)	—	—

a) All T_1 values are in seconds, and values in parentheses are the percentage decrease in the T_1 value when the ligand is complexed by the indicated cation([MSCN]/[crown ether]=1). K_s is the binding constant in 90% MeOH : H_2O (w/w).

Table 2. ^{13}C NMR Relaxation Times (T_1) for Monoaza-18-crown-6, Bis(monoaza-18-crown-6)s, and Their Cation Complexes in 90%(w/w) Methanol Aqueous Solution[a)]

Crown	Cation	logK_s	C-1	C-2	C-3	C-4	C-5	CH_3
CA18C6	None	—	1.02	0.73	1.09	3.18	2.34	4.07
	Na$^+$	2.98	0.77(25%)	0.92(−26%)	0.63(42%)	3.15(1%)	2.06(12%)	4.17(−3%)
	K$^+$	4.17	0.51(50%)	0.46(37%)	0.74(32%)	2.43(24%)	2.09(11%)	4.06(<1%)
BCA18C6	None	—	0.77	0.53	0.35	0.52	0.64	—
	Na$^+$	3.10	0.46(40%)	0.43(19%)	0.46(−31%)	0.45(14%)	0.45(30%)	—
	K$^+$	4.54	0.43(44%)	0.42(21%)	0.56(−60%)	0.56(−8%)	0.57(11%)	—
BOA18C6	None	—	0.72	0.55	0.55	0.60	—	—
	Na$^+$	3.56	0.58(19%)	0.48(13%)	0.49(12%)	0.58(3%)	—	—
	K$^+$	4.75	0.47(35%)	0.47(15%)	0.46(16%)	0.52(13%)	—	—

a) All T_1 values are in seconds, and values in parentheses are the percentage decrease in the T_1 value when the ligand is complexed by the indicated cation([MSCN]/[crown ether]=1). K_s is the binding constant in 90% MeOH : H_2O (w/w).

trometer computer. At least ten points were included for each T_1 calculation (correlation coefficient $\gamma > 0.98$).

A minimum of three runs were accumulated for each systems, and the relative standard deviations were less than ±10%. The relaxation time of the CH_3OH resonance was used as internal standard, and the values ranged from 12.9 to 14.6 s were in good agreement with literature values.[10] Nuclear Overhauser enhancement (NOE) factors measured were those expected for a predominantly dipole–dipole relaxation (2.6—3.0). The only exceptions were T_1s for the CH_3 carbons in monoazacrown ethers, which exhibited NOE values about 2 due to spin rotational contributions.[10]

Results and Discussion

^{13}C NMR spin-lattice relaxation times (T_1s) for monoazacrown ethers, bis(monoazacrown ether)s, and their cation complexes are summarized in Tables 1 and 2 for the 15- and 18-membered series, respectively. The difference between T_1 values before and after interaction with the designated cations is expressed as the percentage by which the relaxation time dropped. It should be noted that in the present study only the changes in T_1 which are larger than 20% could be considered important and effective for discussions because the relative standard deviation in the measurement is in the range of 1.0—10%.

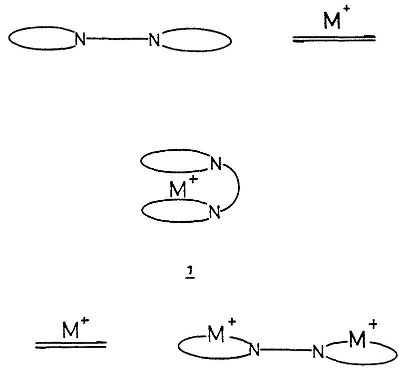
The relaxation times for any given molecule depend upon the molecular mobility (tumbling) and specific motion determined by the internal degrees of freedom of the molecule. Although it is difficult to distinguish these two aspects of the mobility, inferences about the relative motions could be drawn from a careful comparison of the T_1 values for ring carbons (C-1 and C-2) and side-arm carbons (C-3 to C-5) with the corresponding carbons in the closely related systems.

Relaxation Times for Uncomplexed Ligands. As shown in Tables 1 and 2, T_1 values for side-arm carbons of *N*-heptylmonoazacrown ethers, both **CA15C5** and **CA18C6**, are larger than those for their ring carbons, and the terminal methyl carbon shows the largest T_1, as reasonably expected by the location of the carbons in the molecules. Gokel et al. reported that for *N*-butylmonoaza-15-crown-5 the side-arm carbon mobility increases as the distance from the macro ring increases.[10] For both *N*-heptylmonoazacrown ethers here, however, the mobility of C-5 is lower than that of C-4. The fact shows that the side-arm length may affect the specific motion of the carbons in *N*-alkylmonoazacrown ethers. It was reported that T_1 values in $CH_3OH:D_2O$ (9 : 1) for 18-crown-6 (1.28 s) is much smaller than that for 15-crown-5 (2.14 s).[10] However the T_1 values of **CA18C6** and **CA15C5**, for both ring carbons and side-arm carbons, are relatively close.

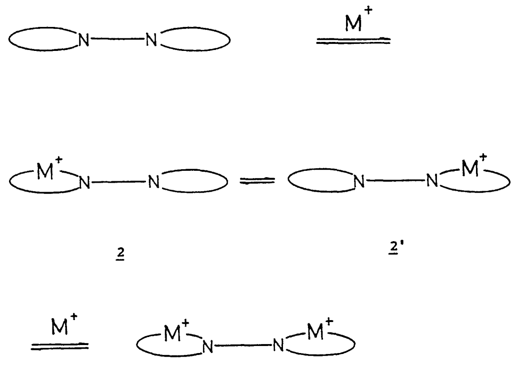
The mobility of bis(monoazacrown ether)s is depressed considerably in comparison with that of corresponding monocyclic analogues for both ring carbons and side-arm carbons. Especially, the T_1 values for bridging chain carbons of bis(monoazacrown ether)s are much smaller than those for side-arm carbons of the monoazacrown ethers. Since the crown ether unit would be strongly solvated by the solvent, it can be reasonably expected that the replacement of the alkyl terminal group in the side arm of **CA15C5** and **CA18C6** by a crown ring as in **BCA15C5** and **BCA18C6**, respectively, will reduce the motion of the whole molecules. It is to be emphasized that the T_1 value of the first bridging carbon (C-3) is the smallest among the all carbons of the bis(monoazacrown ether)s in the tables, and the carbon seems to be a kind of pivot of the molecular motion. Furthermore, the present results indicate that introduction of one oxygen atom into the bridging chain of the bis(monoazacrown ether)s, **BOA15C5** and **BOA18C6**, increases the flexibility of the chain and the mobility of the whole molecule. Especially, the T_1 values for C-3 carbons increase markedly. The result is in line with the deduction about the effect of the chain drawn from the complexation behavior of **BOA15C5** and **BOA18C6**,[9] and a similar result has also been obtained for lariat ethers.[10]

Relaxation Times for Monoazacrown Ether Complexes. The previous study[10] on relaxation times demonstrated that complexation with a cation decreases the mobility of crown ethers, and the decrease of the mobility in *N*-alkylmonoazacrown ethers was larger for ring carbons than for side-arm carbons. For **CA15C5** complexes in Table 1, the K^+-binding gave a larger effect on the mobility of the whole molecule than the Na^+-binding did, although the binding ability of **CA15C5** with Na^+ is a little larger than that with K^+ and the both complexes exist in 1 : 1 stoichiometry.[9] The decrease in T_1 upon the complexation is considered to be dependent not only on the affinity of the crown ether to the cation but also on the structure of the complex formed. The location of larger K^+ ion above the **CA15C5** ring may cause an additional decrease of the T_1s of the ring carbons since the cation should be more strongly solvated at such a position than within the crown ring. For the complex of K^+-**CA18C6**, the large affinity of the complex may explain the large decrease in T_1 values of C-1, C-2, C-3, and even C-4. As an exception, C-2 of Na^+-**CA18C6** complex showed an increase in T_1. For the complex of a large crown ether with a small cation, this result is not unreasonable since such an increase in T_1 was also found for Li^+ and Na^+ complexes of cryptands, and explained by distortion or compression of the ligand by the cations having the small sizes and high charge densities.[11]

Relaxation Times for Bis(monoazacrown ether) Complexes. At the condition of [crown ether]= [cation], two types of complex may exist mainly for bis(monoazacrown ether)s. One is the so-called 'intramolecular sandwich', complex **1** in Scheme 2, in



Scheme 2.



Scheme 3.

which one cation interacts with the two crown units of one bis(crown ether) simultaneously. In another complex, however, the cation interacts only with one crown ring of the bis(crown ether), complex **2** or **2′** in Scheme 3, although there may be a fast equilibrium between the complexes **2** and **2′**. We expected that if the sandwich complex (**1**) is dominant a large decrease in T_1 should be observed for the bridging chain carbons of the bis(monoazacrown ether)s upon the complexation, since the motion of the chain will be limited greatly in such a complex. On the other hand, if most of the complex exists as the complex **2**, the decrease in mobility of the bridging chain carbons will be relatively small. From the results in Tables 1 and 2 we can see that bridging chain carbons C-4 and C-5 of **BCA15C5** and **BCA18C6** show a decrease in T_1 upon the complexation with Na$^+$, but for K$^+$ complexes of **BCA15C5** and **BCA18C6** the decreases in T_1 values of the two carbons are relatively small. It is noticeable that the Na$^+$-binding of **BCA15C5** and **BCA18C6** gives a larger effect than K$^+$-binding on the mobility of the bridging chain carbons, in contrast to the results for the monocyclic analogues (**CA15C5** and **CA18C6**), in which, the decreases in T_1 of both ring carbons and side-arm carbons for K$^+$ complexes are larger than those for Na$^+$ complexes. The behavior of C-3 for **BCA15C5** and **BCA18C6** is very interesting. Upon the complexation with Na$^+$ and K$^+$ the T_1 value of C-3 for **BCA15C5** is almost unchanged, while for **BCA18C6** the T_1 value increases markedly. As mentioned above the mobility of C-3 is considerable constrained in the free bis(monoazacrown ether)s, especially in **BCA18C6,** because of its pivot-like behavior in the motion of whole molecule. The T_1 behavior of the carbons seems to imply that the cation-binding changes moving pattern of the whole molecule and produces a recovery of the mobility of C-3 carbons in

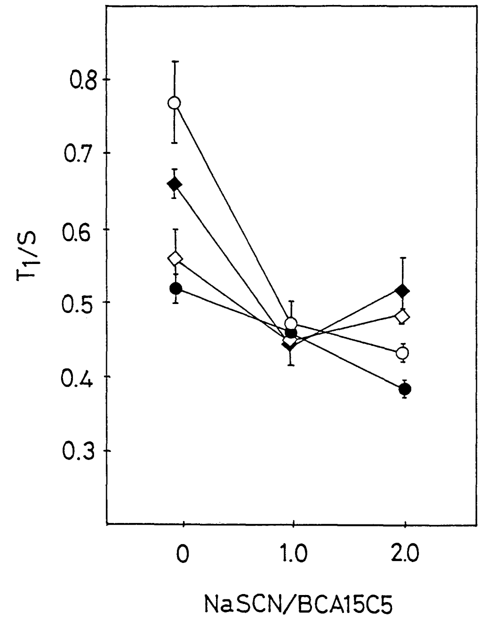


Fig. 1. Influence of added NaSCN on the ^{13}C NMR T_1 values of **BCA15C5**. ○, C-1; ●, C-2; ◇, C-4; ◆, C-5.

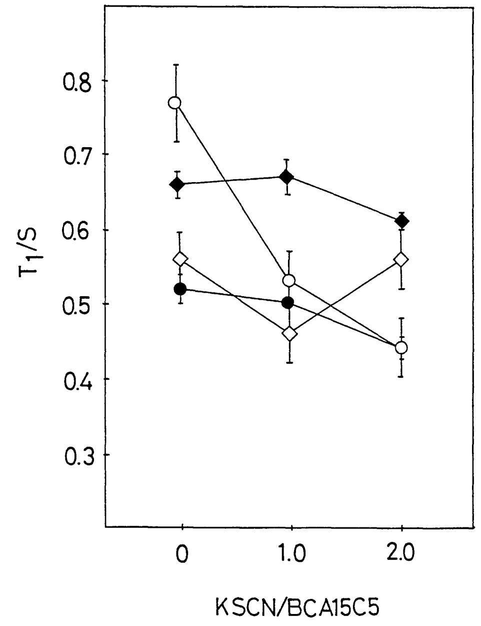


Fig. 2. Influence of added KSCN on the ^{13}C NMR T_1 values of **BCA15C5**. ○, C-1; ●, C-2; ◇, C-4; ◆, C-5.

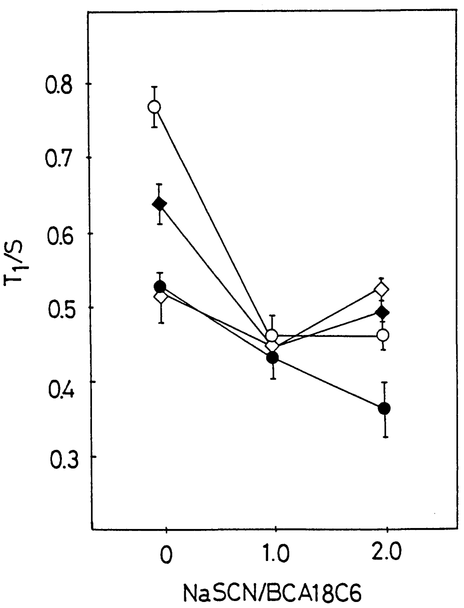


Fig. 3. Influence of added NaSCN on the ^{13}C NMR T_1 values of **BCA18C6**. ○, C-1, ●, C-2; ◇, C-4; ◆, C-5.

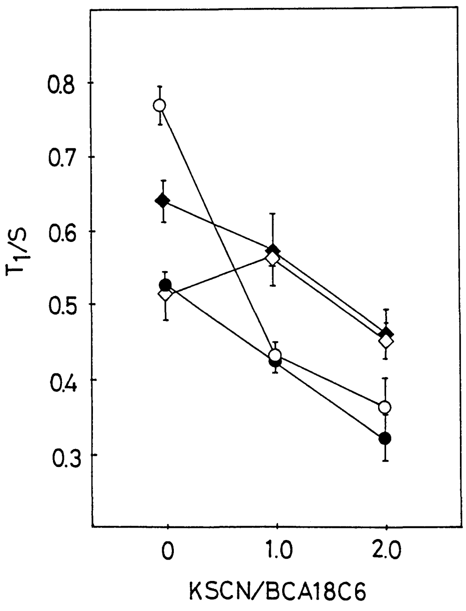


Fig. 4. Influence of added KSCN on the ^{13}C NMR T_1 values of **BCA18C6**. ○, C-1, ●, C-2; ◇, C-4; ◆, C-5.

the complexes of **BCA15C5** and **BCA18C6**.

Figures 1, 2, 3, and 4 show the cation-concentration dependence of the T_1 values for complexes Na^+-**BCA15C5**, Na^+-**BCA18C6**, K^+-**BCA15C5**, and K^+-**BCA18C6**, respectively. For [MSCN]/[crown ether]= 0 and 1 the data in Tables 1 and 2 were used. The error-bar in the figures represent the standard deviation for each datum point. From these figures we can see that the T_1 values for ring carbons (C-1 and C-2) decrease monotonously as the concentration of metal cations increases, but the situation is more complicated for bridging chain carbons. As shown in Scheme 2, in the presence of excess metal cations the sandwich complex would turn to the 2:2 (crown unit:cation) complex, so that the mobility of the bridging chain carbons will recover partially. Thus, the T_1 values of the bridging chain carbons (C-4 and C-5) show a minimum at [NaSCN]/[crown ether]=1, as can be seen in the case of the complexes of Na^+-**BCA15C5** and Na^+-**BCA18C6**. On the other hand, for K^+-**BCA18C6** complex there is no such a minimum in the T_1 profile of the bridging chain carbons. The result suggests that **BCA18C6** does not form the intramolecular sandwich complex with K^+ ion, and is consistent with the result reported before.[9] For K^+-**BCA15C5** complex (Fig. 2) the T_1 value for C-5 is almost unchanged upon the complexation, but C-4 shows a minimum in T_1 profile. Another feature observed in both Na^+-**BCA15C5** and Na^+-**BCA18C6** complex is the fact that all carbon atoms measured show very close T_1 values at [NaSCN]/[crown ether]= 1. The result seems to imply the presence of molecular isotropicity and pseudo-spherical symmetry in these complexes, and is in agreement with the structure of the intramolecular sandwich complex (**1** in Scheme 2). From these results we conclude that the intramolecular sandwich complex is formed in Na^+-**BCA15C5** and Na^+-**BCA18C6** but not in K^+-**BCA18C6**. Apparently, Na^+, whose charge-to-size ratio (Q/r) is larger than that of K^+, strongly organizes the ligand structure and its solvation shell, which may favor the formation of the intramolecular sandwich complex for the flexible bis(monoazacrown ether)s. K^+-**BCA15C5** complex seems to be an intermediate case. Although **BCA15C5** should form the intramolecular sandwich complex with K^+ ion as expected from the size-fit concept, and the existence of such a complex in solution has been shown by other methods,[9] the restriction of K^+ ion to the two crown rings may be relatively weak as compared to Na^+ ion, so that T_1 behavior here could not give clear evidence for the sandwich complex.

The T_1 data for the complexes of **BOA15C5** and **BOA18C6** are also shown in Tables 1 and 2. The previous studies[9] on two-phase extraction and the binding constants in homogeneous solution indicated that the oxygen atom in the bridging chain of the two bis(monoazacrown ether)s can interact directly with the cation held in the ring, and the behavior of the oxygen is very similar to the additional donor atom in the lariat ethers.[15,16] A crystal structure study in the solid state also supported the conclusion.[17] From T_1 data here we can find that the effect of Na^+- and K^+-binding on the T_1 values of **BOA15C5** and **BOA18C6** is very close for both ring carbons and bridging carbons in contrast to that in the complexes of **BCA15C5** and **BCA18C6**. Moreover, the difference of the T_1 values between C-2 and C-3 and that between C-1 and

C-4 in a limited extent, is very small for both **BOA15C5** and **BOA18C6** complexes. These results give clear evidence for participation of the bridging chain oxygen to the coordination. Thus, the oxyethylene moiety in the bridging chain can be considered to behave as a part of the ring neighboring to the nitrogen in the complexation in these complexes, and the complexes may take an analogous partial structure around a cation to lead the observation that mobility of the ring carbons and bridging chain carbons become very close. Interestingly, the decrease in T_1 values of the bridging chain carbons (C-3 and C-4) of **BOA15C5** and **BOA18C6** upon the complexation is not so large in comparison with the result reported by Gokel et al.[10] in which a large decrease in T_1 values could be observed for side-arm carbons of lariat ethers in Na^+ complexes. This is reasonably explained by the fact that the mobility of the bridging chain of the bis(crown ether) is rather restricted by the two terminal crown rings even in the free form and may be also affected by the coordination of the oxygen in the chain to the same extent with that of the ring carbons (C-1 and C-2). It is clear that the participation of the bridging chain oxygen to the complexation plays a decisive role in the mobility of the **BOA15C5** and **BOA18C6** complexes, and makes it difficult to discriminate the formation of the intramolecular sandwich structure for these complexes.

Conclusion

^{13}C NMR relaxation times study of the bis(monoazacrown ether)s demonstrated that **BCA15C5** and **BCA18C6** can form an intramolecular sandwich complex with Na^+ ion. For the complexation with K^+ ion, however, there is no clear evidence for the formation of such a complex. The results from the complexes of flexible bis(monoazacrown ether)s are attributable to the nature of Na^+ ion, which has a large charge-to-size ratio (Q/r) and can strongly organize the ligand structure and the solvation shell. For the complexation of **BOA15C5** and **BOA18C6,** the observed T_1 values seem to be controlled markedly by the structure including the coordination of the oxygen in the bridging chain. However, further information about the whole structure of these two complexes could not be obtained by the present experiment.

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