New Applications of Crown Ethers. Part 8.[1] Complexation of Bis(monoaza-crown ether)s with Alkali-metal Cations

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The complexation behaviour of bis(monoazacrown ether)s (BCA15C5, BCA18C6, BOA15C5, BOA18C6) with alkali-metal cations was studied by means of solvent extraction, stability constants in homogeneous solution, and ^{13}C n.m.r. spectroscopy. Bis(monoaza-18-crown-6)s, BCA18C6 and BOA18C6, cannot form an intramolecular sandwich complex with K^+, probably because of the stability of the macrorings in pseudo-D_{3d} conformation, and also of preferential donation of the oxygen atom in the bridging chain in BOA18C6, as in 'lariat ethers'. For bis(monoaza-15-crown-5), especially for BOA15C5, the existence of the intramolecular sandwich structure was found both in Na^+ and K^+ complexes. It is presumed that the more flexible monoaza-15-crown ring does not suffer from restraint in the formation of the sandwich structure, and the oxygen atom in the bridging chain not only increases the flexibility of the chain but also can co-ordinate directly with the cation held in the sandwich cavity.

The most notable property of macrocyclic polyether ligands (crown ethers) is size recognition in complexation with metal cations.[2] Bis(crown ether)s consisting of two crown rings in one molecule can hold a cation larger than the hole size of the crown unit, and have much higher binding ability than their monocyclic analogues, the so-called 'biscrown effect'.[3-6] In the previous Parts the synthesis and complexation of substituted benzocrown ethers and bis(benzocrown ether)s were discussed.[4,7] The fit of the hole size to the cation diameter is a crucial factor for the preferential complexation of K^+ by benzo-18-crown-6 and of Cs^+ by benzo-21-crown-7. Bis(benzo-15-crown-5)s and bis(benzo-18-crown-6)s formed an intra-molecular sandwich complex with K^+ and Cs^+, respectively, but bis(benzo-21-crown-7)s did not form such a sandwich complex with any alkali-metal cation. The presence of oxygen atom(s) in the side or the bridging chain gives only a moderate effect on the complexation in these mono- and bis-benzocrown ethers.

In monoazacrown ethers carrying a flexible side-chain with one or more oxygen atoms, 'lariat ethers', the extra co-ordination by the oxygen atom(s) considerably increases the binding ability of the ethers with cations, the so-called 'lariat effect'.[8,9] Sutherland. reported the different features of monoazacrown ethers and bis(monoazacrown ether)s in complexation with ammonium ion using a ^1H n.m.r. method.[10] Bis(monoaza-15-crown-5)s can form only the intramolecular sandwich complex with a bis(alkylammonium ion) but bis(monoaza-18-crown-6)s form both the intramolecular and intermolecular complexes. The results prompted us to examine the complexation of bis(monoazacrown ether)s with alkali-metal cations. In Part 7,[1] we found that bis(crown ether)s consisting of a benzocrown unit and a monoazacrown unit cannot form an intramolecular sandwich complex with alkali-metal cations as do bis(benzocrown ether)s, and bind the cations like lariat ethers. Here we describe the complexation of bis(monoazacrown ether)s with alkali-metal cations in both two-phase and homogeneous solution.

Experimental

Materials.—*N*-Substituted monoazacrown ethers (Scheme 1) were prepared according to published methods.[8,9,11] Methylene dichloride was purified by successive washing with concentrated H_2SO_4, aqueous alkaline solution, and distilled water, and was dried ($CaCl_2$). After distillation, it was saturated with distilled water before use. Methanol was distilled and diluted with distillated water to give 90% (w/w) methanol aqueous solutions. Samples of alkali-metal chlorides, alkali-metal hydroxides, alkali-metal thiocyanates, and picric acid were not further purified except for drying.

Bis(monoazacrown ether)s. The bis(monoazacrown ether)s were prepared with the methods of Sutherland *et al.* as described briefly in Scheme 1.[10] The purity and structure of the crown ethers were confirmed by i.r., n.m.r., mass spectra, and elemental analysis.

1,5-*Bis*-(N-*monoaza*-15-*crown*-5)*pentane* (BCA15C5) was an oil, b.p. 160—175 °C at 0.003 Torr (Found: C, 59.2; H, 9.9; N, 5.45. $C_{25}H_{50}N_2O_8$ requires C, 59.3; H, 9.95; N, 5.5%); $v_{max.}$(neat) 1 130 cm^{-1} (O–C); δ_H(60 MHz; CDCl$_3$) 1.2—1.7 (6 H, m, CH$_2$CH$_2$CH$_2$), 2.5—3.0 (12 H, t, CH$_2$N), and 3.2—4.0 (32 H, m, CH$_2$CH$_2$O); m/e 506 (M$^+$).
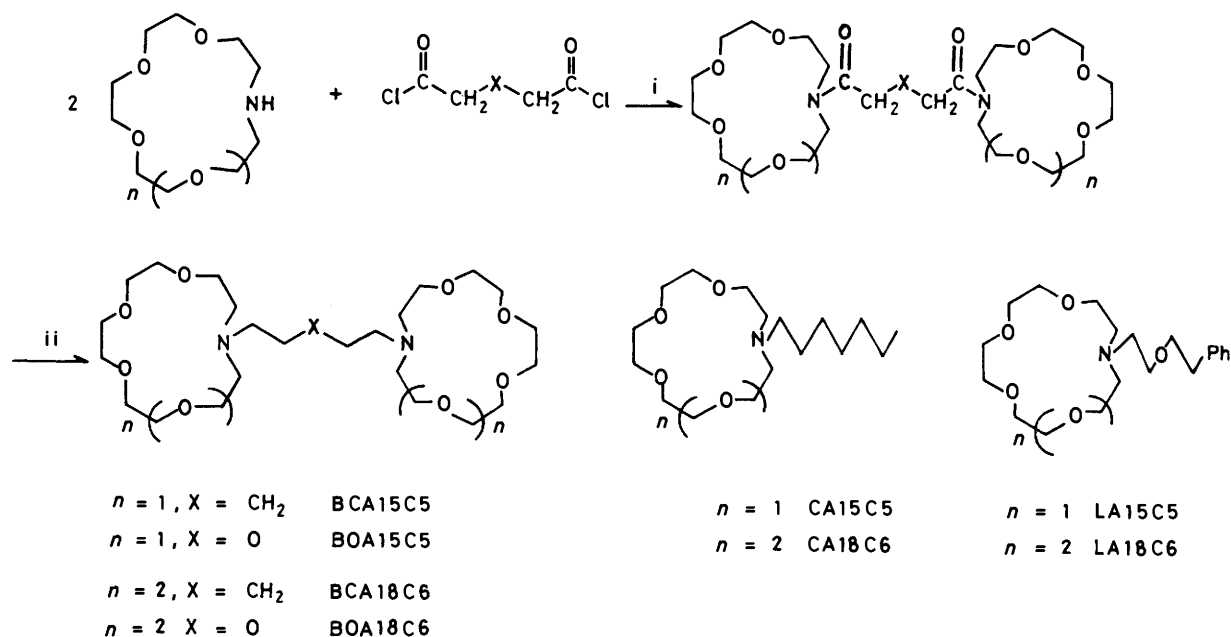
1,5-*Bis*-(N-*monoaza*-18-*crown*-6)*pentane* (BCA18C6) was an oil, b.p. 185—195 °C at 0.004 Torr (Found: C, 58.3; H, 9.8; N, 4.7. $C_{29}H_{58}N_2O_{10}$ requires C, 58.55; H, 9.8; N, 4.7%); $v_{max.}$(neat) 1 130 cm^{-1} (O–C); δ_H(60 MHz; CDCl$_3$) 1.2—1.7 (6 H, m, CH$_2$CH$_2$CH$_2$), 2.5—3.0 (12 H, t, CH$_2$N), and 3.2—4.0 (40 H, m, CH$_2$CH$_2$O); m/e 594 (M$^+$).

1,5-*Bis*-(N-*monoaza*-15-*crown*-5)-3-*oxapentane* (BOA15C5) was an oil, b.p. 160—170 °C at 0.004 Torr (Found: C, 57.0; H, 9.6; N, 5.4. $C_{24}H_{48}N_2O_9$ requires C, 56.7; H, 9.5; N, 5.5%); $v_{max.}$ 1 120 cm^{-1} (O–C); δ_H(60 MHz; CDCl$_3$) 2.5—3.0 (12 H, t, CH$_2$N) and 3.2—3.9 (39 H, m, CH$_2$CH$_2$O); m/e 508 (M$^+$).

1,5-*Bis*-(N-*monoaza*-18-*crown*-6)-3-*oxapentane* (BOA18C6) was an oil, b.p. 190—200 °C at 0.004 Torr (Found: C, 56.4; H, 9.5; N, 4.7. $C_{28}H_{56}N_2O_{11}$ requires C, 56.4; H, 9.5; N, 4.7%); $v_{max.}$(neat) 1 120 cm^{-1} (O–C); δ_H(60 MHz; CDCl$_3$) 2.5—3.0 (12 H, t, CH$_2$N) and 3.2—3.9 (36 H, m, CH$_2$CH$_2$O); m/e 596 (M$^+$).

Solvent Extraction.—Solvent extraction was carried out with alkali-metal picrates in methylene dichloride–water.[12] The percentage of picrate salt extracted (Ex%) was based on the picrate concentration in the aqueous phase after equilibration under the following conditions: CH$_2$Cl$_2$ = H$_2$O = 10 ml, [picric acid] 7 × 10^{-5}M, [M(OH)] 0.01M, [crown unit] 3.5 × 10^{-4}M at 25 °C.
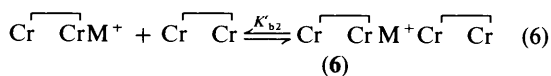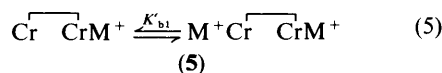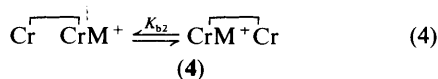
Stability Constants.—Stability constants were determined for a mixture of 2.5 × 10^{-4}—8.0 × 10^{-4}M-crown unit and 4.0 × 10^{-4}—2.0 × 10^{-3}M-metal chloride in 90% (w/w) methanol

$n = 1, X = CH_2$ BCA15C5
$n = 1, X = O$ BOA15C5

$n = 2, X = CH_2$ BCA18C6
$n = 2 \; X = O$ BOA18C6

$n = 1$ CA15C5
$n = 2$ CA18C6

$n = 1$ LA15C5
$n = 2$ LA18C6

Scheme 1. *Conditions:* i, room temperature, 2 h, CH_2Cl_2, Et_3N; ii, $LiAlH_4$, THF

aqueous solution at 25 °C by measuring the e.m.f. for the respective electrode [Na⁺ − ISE(TOA NA-115B) for Na⁺, and monovalent cation electrode (Corning Cat. 476220) for K⁺ and Cs⁺] against an Ag–AgCl reference electrode using an Orion Research model 701A digital Ionanalyzer, as previously described.[13]

For mono(crown ether)s the stability constants can be defined by equations (1) and (2) and those for bis(crown ether)s by equations (3)—(6).[4,14] We determined K_{1obs} and K_{2obs} by

$$M^+ + Cr \xrightleftharpoons{K_{m1}} M^+Cr \qquad (1)$$

$$M^+Cr + Cr \xrightleftharpoons{K_{m2}} CrM^+Cr \qquad (2)$$

$$Cr\;Cr + M^+ \xrightleftharpoons{K_{b1}} Cr\;CrM^+ \qquad (3)$$

$$Cr\;CrM^+ \xrightleftharpoons{K_{b2}} CrM^+Cr \qquad (4)$$

$$Cr\;CrM^+ \xrightleftharpoons{K'_{b1}} M^+Cr\;CrM^+ \qquad (5)$$

$$Cr\;CrM^+ + Cr\;Cr \xrightleftharpoons{K'_{b2}} Cr\;CrM^+Cr\;Cr \qquad (6)$$
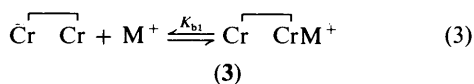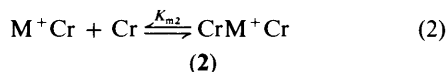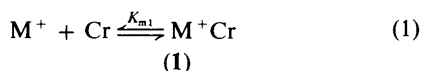
varying the concentration of the crown ether or of the cation, and calculated them from regression analysis. For mono(crown ether)s, equations (7) and (8) hold and for bis(crown ether)s,

$$K_{1obs} = K_{m1} \qquad (7)$$

$$K_{2obs} = K_{m2} \qquad (8)$$

$$K_{1obs} = \frac{[Cr\;CrM^+] + [CrM^+Cr]}{[Cr\;Cr][M^+]} = K_{b1}(1 + K_{b2}) \qquad (9)$$

$$K_{2obs} = \frac{[M^+Cr\;CrM^+]}{([Cr\;CrM^+] + [CrM^+Cr])[M^+]} = \frac{K'_{b1}}{1 + K_{b2}} \qquad (10)$$

(9) and (10). Since the intermolecular sandwich complex (6) was not significant under the present conditions ([M⁺] > [Cr Cr]), K'_{b2} was not considered in the analysis.

[13]*C N.m.r. Spectra.*—A typical sample was prepared by weighing a fixed amount of the ligand (0.1 g, 0.31—0.40 mmol) in a 5 mm o.d. n.m.r. tube, addition of MSCN (NaSCN or KSCN) with a ratio [MSCN]:[Cr unit] of 0.25—3.0, and dissolution of the mixture with CD_3OD (0.4 ml). Natural-abundance [13]C n.m.r. spectra were recorded on a JEOL FX-90-Q spectrometer, operating at 22.5 MHz. The pulse width used was 6 s (45°). The spectral window was 4 000 or 5 000 Hz and the acquisition time 0.91 s with 8 K data points. Delays of 5 s were used after each pulse-acquisition sequence. The spectra were obtained under proton noise decoupling conditions, and the chemical shifts were determined by using tetramethylsilane as internal standard with an accuracy in the measurements of ±0.07 p.p.m.

Results and Discussion

Solvent Extraction.—We previously showed that the results for percentage of picrate salt extracted (Ex%) from the solvent extraction are essentially parallel to those for extraction equilibrium constants (K_e).[4] In fact it is difficult to compare directly the K_e values of bis(crown ether)s with those of mono(crown ether)s. In this report, therefore, Ex% is still used for comparison of the behaviour of bis(monoazacrown ether)s with that of monoazacrown ethers although the value represents a combined effect of many factors.

The results of the solvent extraction are summarized in Table 1, and also in Figures 1 and 2 in which Ex% is plotted against

Table 1. Extraction of alkali-metal picrates[a]

Crown ether	Extracted picrate salts (%)				
	Li^+	Na^+	K^+	Rb^+	Cs^+
CA15C5[b]	1.4	20.8	4.2	1.6	3.2
LA15C5[b]	14.0	52.8	42.5	21.6	15.7
BCA15C5	4.4	33.1	26.0	36.4	25.6
BOA15C5	26.6	81.0	93.6	94.3	89.9
	(18.6)	(64.1)	(81.2)	(83.0)	(73.3)
CA18C6[b]	4.0	17.0	79.0	53.5	25.9
LA18C6[b]	10.0	58.4	95.5	90.0	65.4
BCA18C6	8.5	21.1	81.0	58.1	33.7
BOA18C6	15.8	59.6	95.0	88.3	75.6
	(8.1)	(37.4)	(76.3)	(64.4)	(49.2)

[a] CH_2Cl_2 = H_2O = 10 ml. Aqueous phase: [Picric acid] 7.0 × 10^{-5}M, [Metal hydroxide] 0.01M. Organic phase: [Crown unit] 3.5 × 10^{-4}M. The values in parentheses are for [Crown unit] 1.75 × 10^{-4}M. [b] Ref. 1.
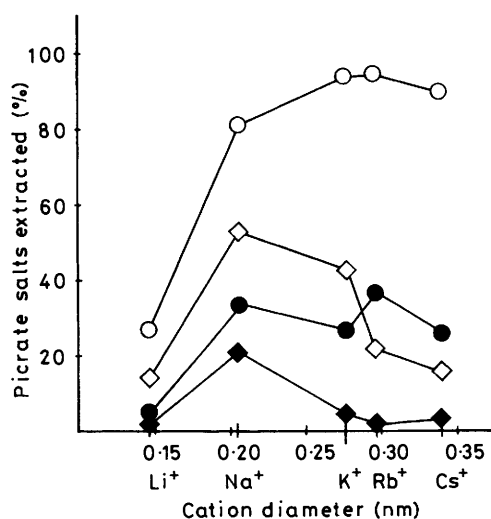

Figure 1. Extraction of alkali-metal picrates with monoaza-15-crown-5 series: ◆, CA15C5; ◇, LA15C5; ●, BCA15C5: ○, BOA15C5. The data in Table 1 are plotted

the cation diameter. Tying the two monoazacrown rings gave very different effects in extraction between the 15- and 18-membered ring systems. BCA15C5 exhibited an enhancement of Ex% compared with its monocyclic analogue, CA15C5, and its selectivity changed for larger cations, e.g. Rb^+. The result may be explained by the formation of an intramolecular sandwich complex as in the case of bis(benzocrown ether)s. However, BCA18C6 showed almost the same extraction behaviour as its monomer, CA18C6. The oxygen atoms in the bridging chain increase the extraction ability for both 15- and 18-membered ring systems, but the effect on the extraction differs considerably between them. The extraction behaviour of BOA18C6 is very similar to that of LA18C6, but Ex% for BOA15C5 is much larger than that of LA15C5 through Li^+ to Cs^+. As shown in previous parts,[1,4] the distribution constant (P_e) of the crown ethers affects the extraction equilibrium constant (K_e) by a factor of $(1 + P_e)$. However, the marked differences of Ex% in the pairs, BCA15C5–CA15C5 and BOA15C5–LA15C5, could not be explained only by some increase in P_e values for the bis(monoazacrown ether)s.*

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* The distribution constants (P_e) of LA15C5 and LA18C6 are 0.17 and 0.11, respectively.[1] The other crown ethers used may be expected to have similar or slightly larger P_e values although we failed to determine them accurately by a simple method.
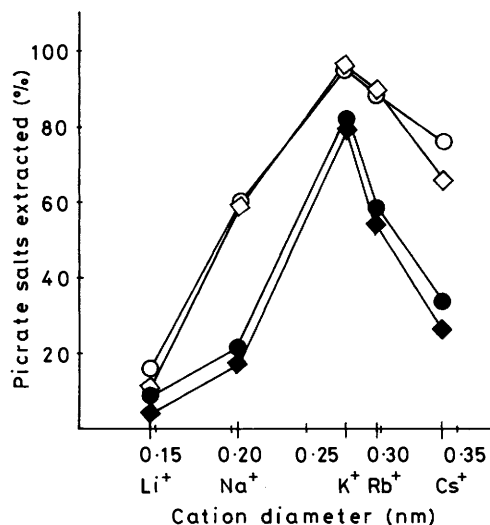

Figure 2. Extraction of alkali-metal picrates with monoaza-18-crown-6 series: ◆, CA18C6; ◇, LA18C6; ●, BCA18C6; ○, BOA18C6. The data in Table 1 are plotted

Homogeneous Stability Constants.—In order to clarify the unexpected behaviour of the bis(monoazacrown ether)s in solvent extraction, stability constants in homogeneous solution were determined for complexation with alkali-metal cations in 90% (w/w) methanol aqueous solution. In the present study three types of crown ether–cation complexes were considered for bis(monoazacrown ether)s to calculate the stability constants described in equations (3)—(5). The results are shown in Table 2 as the observed stability constants K_{1obs} and K_{2obs} along with those for the corresponding monocyclic species. It should be noted that K_{1obs} and K_{2obs} for bis(crown ether)s are defined very differently from those for mono(crown ether)s as shown in equations (7)—(10). Equations (9) and (10) show that the formation of the intramolecular sandwich complex (4) would cause an increase in K_{1obs} and a decrease in K_{2obs} for bis(crown ether)s, and the changes were indeed the case observed in bis(benzocrown ether)s.[4]

In homogeneous solution, unfortunately, the 'biscrown effect' for bis(monoazacrown ether)s is not so clear as for bis(benzocrown ether)s, but we can still elucidate the following facts from Table 2. In complexation with Na^+, a negligible K_{2obs} suggests that the bis(monoazacrown ether)s, both 15- and 18-membered ring systems are able to form the intramolecular sandwich complex (4). While a larger K_{2obs} means the formation of the 2:2 crown unit–cation complex (5) in their Cs^+ complexes. Bis(monoaza-15-crown-5)s and bis(monoaza-18-crown-6)s exhibited very different behaviour in complexation with K^+, and the results are consistent with those from solvent extraction. The formation of the intramolecular sandwich complex (4) can be observed in BCA15C5–K^+ and BOA15C5–K^+. However bis(monoaza-18-crown-6)s BCA18C6 and BOA18C6 bind K^+ as the 2:2 crown unit–cation complex (5) instead of the intramolecular sandwich one (4), although their monocyclic analogues, CA18C6 and LA18C6, can sandwich K^+ intermolecularly. The presence of the oxygen atom in the bridging chain increases the binding ability of BOA15C5 and BOA18C6 compared with that of BCA15C5 and BCA18C6, respectively. An especially large increase in K_{1obs} can be found where the intramolecular sandwich complex forms.

[13]C *N.m.r. Study.*—Dale *et al.* used [13]C n.m.r. spectroscopy to study conformational change in complexation of various crown

Table 2. Complexation stability constants in H_2O–MeOH (1:9 w/w)[a]

Crown ether	Na+		K+		Cs+	
	$\log K_{1obs}$	$\log K_{2obs}$	$\log K_{1obs}$	$\log K_{2obs}$	$\log K_{1obs}$	$\log K_{2obs}$
CA15C5[b]	2.76 ± 0.04	c	2.29 ± 0.03	c	2.71 ± 0.01	c
CA18C6[b]	2.98 ± 0.12	c	4.17 ± 0.01	3.21 ± 0.21	3.53 ± 0.08	c
LA15C5[b]	3.43 ± 0.03	c	3.64 ± 0.03	3.34 ± 0.10	3.15 ± 0.09	c
LA18C6[b]	3.48 ± 0.01	c	4.78 ± 0.06	3.96 ± 0.26	3.82 ± 0.01	c
BCA15C5	2.82 ± 0.03	c	2.69 ± 0.10	c	3.07 ± 0.04	3.78 ± 0.05
BCA18C6	3.10 ± 0.06	c	4.54 ± 0.03	3.08 ± 0.06	3.36 ± 0.07	3.37 ± 0.07
BOA15C5	3.63 ± 0.05	c	3.70 ± 0.08	c	3.42 ± 0.01	3.10 ± 0.03
BOA18C6	3.56 ± 0.07	c	4.75 ± 0.20	3.07 ± 0.09	3.66 ± 0.01	3.14 ± 0.08

[a] [Metal chloride] 4.0×10^{-4}—2.0×10^{-3}M and [Crown unit] 2.5×10^{-4}—8.0×10^{-4}M in 90% MeOH aqueous solutions at 25 °C, see text. [b] Ref. 1. [c] The standard deviation of K_{1obs} was <10% in one group measurement, no regression analysis was done in calculating K_{2obs}.

ethers in solution.[15,*] They observed that upon complexation almost all the carbons of the cyclic oligomers used gave upfield shifts in ^{13}C n.m.r., and concluded that the degree of upfield shift on the complexation depends primarily on the type of conformational changes needed to form the complex. It can reasonably be expected that a special conformational change in the formation of the intramolecular sandwich complex (4) would be reflected in the ^{13}C n.m.r. chemical shifts. Thus we investigated the ^{13}C n.m.r. shifts of the bis(monoazacrown ether)s in complexation with NaSCN and KSCN. The changes in the chemical shift of C-5 and -6 of the crown ethers (see Scheme 2) upon the complexation is plotted against the ratio of
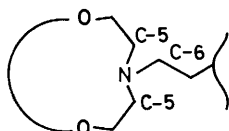
Scheme 2.

[MSCN]:[Cr unit] in Figures 3 and 4 ($\Delta\delta = \delta_{M^+} - \delta_O$). The other carbon atoms of the crown ethers could not be assigned clearly in the ^{13}C n.m.r. spectra, and the chemical shift of $MS^{13}CN$ was unaffected by complexation. The chemical shifts determined here are the average values for the uncomplexed and complexed ligands which may exist in several types. The contribution of the intramolecular sandwich complex (4) is considered to be large only when [MSCN]:[Cr unit] is small, since a further increase of [MSCN]:[Cr unit] give rise to the formation of 2:2 crown unit–cation complex (5).

Three interesting points can be seen in Figures 3 and 4. First, the magnitude of the change in ^{13}C n.m.r. chemical shift for C-5 is smaller than that of the side-chain C-6 upon complexation with Na+ and K+. This observation is in agreement with the conclusion of Dale et al. that these changes are attributed to the conformational changes of crown ethers in their cation complexation. Secondly, in BOA15C5–Na+, BCA15C5–K+, BOA15C5–K+, and BOA18C6–Na+ systems there is a biphasic change (initial shift to downfield then to upfield) in the low [MSCN]:[Cr unit] range of the $\Delta\delta$–[MSCN]:[Cr unit] profile. BOA15C5–K+ shows a maximum in the profiles of both C-5 and -6, while similar phenomena were not observed in monoazacrown ethers nor in lariat monoazacrown ethers.[17] The presence of such peculiar chemical shifts could be reasonably understood by the existence of different conformations in low and high [MSCN]:[Cr unit] region, and suggests

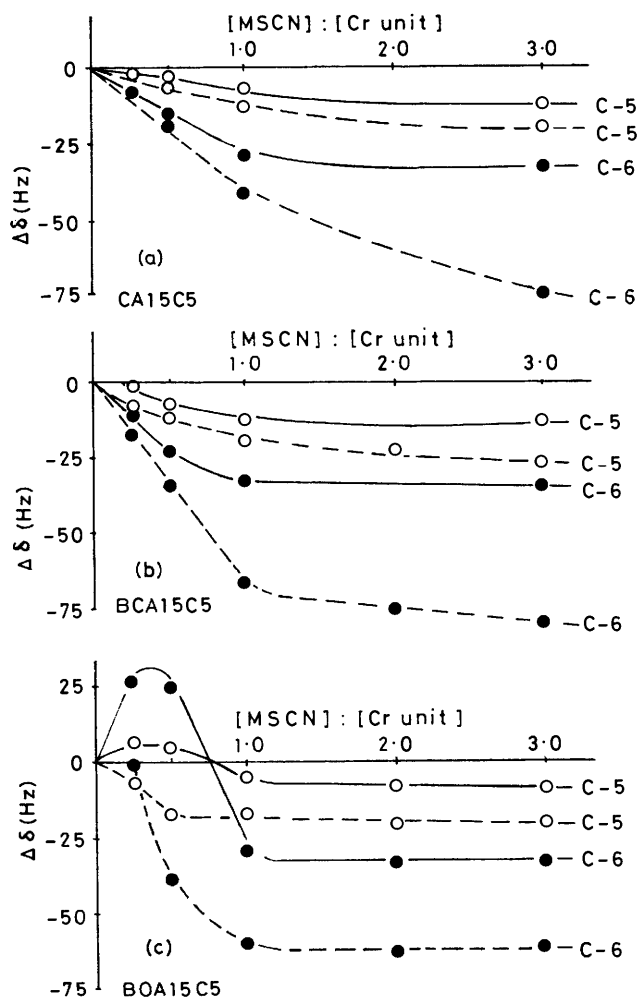*The Na+ complex of bis(monoaza-12-crown-4) has also been studied.[16]

Figure 3. Influence of added MSCN on the ^{13}C n.m.r. chemical shifts of the crown ethers: – – – – NaSCN; ——— KSCN

the formation of the intramolecular sandwich complex (4) in the low [MSCN]:[Cr unit] region. Finally, K+ complexes of CA18C6, BCA18C8, and BOA18C6 exhibit small downfield shifts for C-5 and large upfield shifts (ca. 6 p.p.m.) for C-6, very different behaviour from that in other cases. The similarity of the profiles of BCA18C6–K+ and BOA18C6–K+ with that of CA18C6–K+ supports the absence of the intramolecular sandwich structure in these bis(crown ether) complexes. When these results are combined with those of solvent extraction and
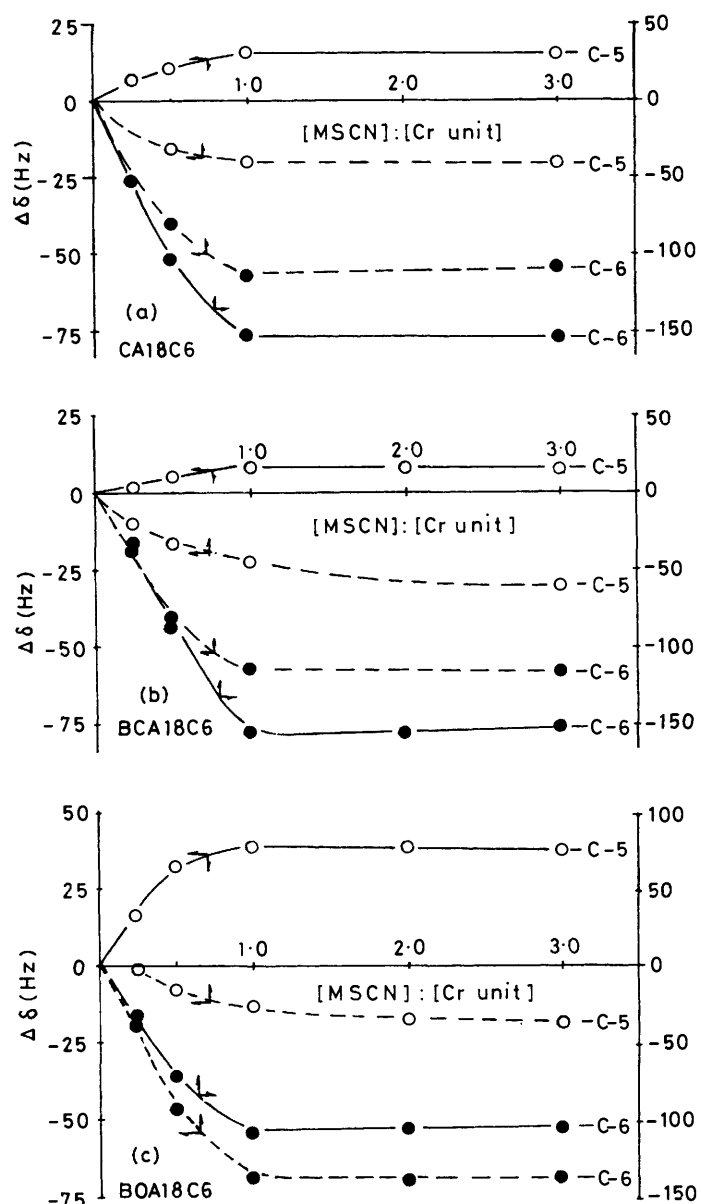
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Figure 5. Schematic presentation of the pseudo-D_{3d} conformation of monoaza-18-crown-6

Figure 4. Influence of added MSCN on the ^{13}C n.m.r. chemical shifts of the crown ethers: – – – – NaSCN, —— KSCN

stability constants, it can be concluded that the intramolecular sandwich complex (4) forms in BCA15C5-K$^+$, BOA15C5-K$^+$, BOA15C5-Na$^+$, and BOA18C6-Ma$^+$, while it does not exist in BCA18C6-K$^+$ and BOA18C6-K$^+$.

The complexation behaviour of the bis(monoazacrown ether)s should be related closely to the nature of the monoazacrown ring. A D_{3d} structure of the 18-crown-6 complex with K$^+$ is well known, in which six donor atoms are disposed in a chair conformation.[16.18] The structure is so stable as to be maintained in complexation with the cations Rb$^+$ and Cs$^+$ which are located above the macro-ring plane in the complexes, but complexation with a small cation, i.e. Na$^+$, of high charge density, can deform the structure.[18,19] A similar chair conformation for the donor atoms was also observed in monoaza-18-crown-6 and in the K$^+$ complex of lariat monoaza-18-crown-6- (pseudo-D_{3d} structure), though the hole size can shrink slightly in the presence of a nitrogen atom.[20,21] The characteristic behaviour observed in ^{13}C n.m.r. chemical shifts of C-5 and -6 of monoaza-18-crown-6 ring may also provide
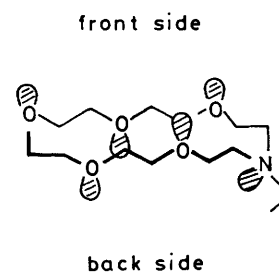
more evidence for the existence of the pseudo-D_{3d} arrangement in the K$^+$ complex. The presence of the pivotal nitrogen in the macro-ring differentiates each side of the ring plane, i.e., one side (front side) with three axial non-bonding lone pairs (n_{ax}) of oxygen, and the other side (back side) with only two n_{ax} (Figure 5).[22] A cation larger than the hole size is expected to be disposed preferably above the front side. In the binding with CA18C6, K$^+$ can be flanked intermolecularly with each front side of the two ligands. For bis(monoaza-18-crown-6)s (BCA18C6 and BOA18C6), however, an examination of CPK models shows that the intramolecular sandwich structure with two front sides is impossible because of the hindrance of the pyramidal structure of the pivotal nitrogen. A similar hindrance is found in the X-ray crystal structure of the K$^+$ complex of lariat monoaza-18-crown-6 in which the N-pivotal lariat arm can co-ordinate the cation only from the back side.[21] This consideration indicates why BCA18C6 and BOA18C6 cannot take the intramolecular sandwich structure in complexation with the larger cations, such as K$^+$, Rb$^+$, and Cs$^+$, both in a two-phase system and homogeneous solution. The close similarity in the extraction behaviour of BCA18C6 and BOA18C6 with their monocyclic analogues may be explained by the formation of the intermolecular sandwich complex (6) and the oxygen atom in the bridging chain of BOA18C6 acts just as in the lariat ethers. On the other hand, for the small cations, Li$^+$ and Na$^+$, the D_{3d} structure may be destroyed in complexation, and bis(monoaza-crown ether)s, both 15- and 18-membered rings, can form the intramolecular sandwich complex (4) with Na$^+$. Thus the 'induced fit' concept seems to be more suitable than the 'lock and key' concept for understanding the complexation behaviour of the bis(monoazacrown ether)s with Na$^+$. In this case, as in the lariat monoazacrown ethers, the macro-rings could solvate in the geometry most appropriate for the cation but not for the macro-ring.[9]

In contrast with monoaza-18-crown-6, there is no favourable D_{3d} arrangement with particular stability in complexation for the 15-membered ring. Owing to the lack of the restriction mentioned above, BCA15C5 and BOA15C5 can assume the intramolecular sandwich structure in complexation. A CPK model study shows that all the donor atoms can face the centre of the sandwich structure formed with bis(monoaza-15-crown-5)s. The consideration is also supported by the results of single-crystal X-ray analyses for the complex of 15-crown-5,[23] benzo-15-crown-5,[24,25] and lariat monoaza-15-crown-5.[26] The oxygen atom in the bridging chain of BOA15C5 not only increases the flexibility of the chain but also co-ordinates directly with the cation held in the sandwich cavity, and the effect may account for the remarkable increase in Ex% for BOA15C5.

In conclusion, bis(monoaza-15-crown-5)s tend to form an intramolecular sandwich complex with alkali-metal cations, and bis(monoaza-18-crown-6)s can assume both intra- and inter-molecular sandwich structures depending upon the type of cation. The conclusion is in accord with Sutherland's results

obtained for complexation with bis(alkylammonium ion)s.[10] The present study also provides an explanation for the fact that little 'biscrown effect' could be observed for the bis(monoaza-18-crown-6) in the liquid membrane cation-transport experiment reported by Shono and co-workers.[27,*]

Acknowledgements

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* There is a recent report on bis(monoazacrown ether)s.[28]

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