

**BIS(MONOAZACROWN ETHERS) WITH AN ELECTRON-DONATING SUBSTITUENT AT THE HINGE: A PRONOUNCED PARTICIPATION OF HYDROXYL GROUP IN FORMATION OF SODIUM ION SANDWICH COMPLEXES\***

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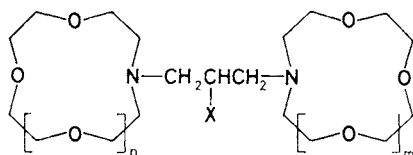
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Sodium ion complex formation has been investigated potentiometrically in four homologous bis(crown) series *I–IV* differing by the nature of substituent placed at the linking trimethylene chain (X = OH, OCH<sub>3</sub>, OCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub> and H respectively). A marked enhancement of the complex stability has been observed in the bis(crown) series *I* and attributed to participation of the lateral hydroxyl group in the sandwich complex formation. Evidence in support of the sandwich structure has been provided (i) by analysis of the potentiometric data indicating a 1 : 1 complex stoichiometry and (ii) by a comparison of the complex stability data from the bis(crown) series *I* with the corresponding values from related monocyclic ligand series *V*, *VI* and *VII* revealing a pronounced cooperation of both macrorings in the sodium ion–bis(crown) *I* complex formation.

Although special complexation properties of bis(crown) compounds have been discussed already at several occasions and attributed in most instances to an intra-



*I*, X = OH

*II*, X = OCH<sub>3</sub>

*III*, X = OCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>

*IV*, X = H

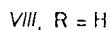
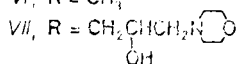
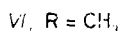
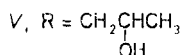
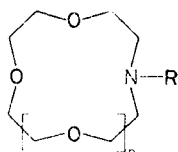
In formulae *I–IV*: *a*, *n* = *m* = 1    *b*, *n* = *m* = 2    *c*, *n* = *m* = 3

*d*, *n* = 1; *m* = 2    *e*, *n* = 1; *m* = 3    *f*, *n* = 2; *m* = 3

\* Part IX in the series *Chemistry of Multidentate Ligands*; Part VIII: Collect. Czech Chem. Commun. 52, 2971 (1987).

molecular sandwich complex formation<sup>1-5</sup>, factors that may take part in control of this particular complexation behaviour remain far from being understood.

In this paper we report results of a potentiometric study of sodium ion complexation in a homologous series of bis(crowns) *Ia–If* bearing one aza-donor site in each macroring\* and a lateral hydroxyl group placed at a trimethylene hinge. At the same time we report complementary potentiometric results from six subsidiary mono-



In formulae V–VIII: a, n = 1    b, n = 2    c, n = 3

and bis(crown) series *Iia–Iic*, *IIia–IIic*, *IVa–IVc*, *Va–Vc*, *VIa–VIc* and *VIIa–VIIc*. Bis(crown) structure – sandwich complex stability relationship is examined on basis of the experimental results.

## EXPERIMENTAL

Bis(crowns) *Ia–If* and their “mini” analogues *VIIa–VIIc* were available from the previous work<sup>7</sup>. Mono-crowns *VIa–VIc* and *VIIIa–VIIIc* were prepared by known procedures<sup>8–11</sup>.

### Bis(crowns) *Iia–Iic*

An appropriate monoazacrown ether *VIIIa–VIIIc* (12 mmol) was stirred under reflux with 1,3-bis-(*p*-toluenesulphonyloxy)-2-methoxypropane (2.48 g; 6 mmol) and anhydrous sodium carbonate (2.0 g; 19 mmol) in dioxane (20 ml) for 10 h. The mixture was diluted with chloroform (50 ml) and the precipitated salts were filtered off. The solvents were taken down on aspirator and the product was isolated by a Kugelrohr distillation or by a column chromatography on alumina (Merck; act. II). Data are in Tables I and II.

\* For a shorthand description of the individual macrorings we use a simplified version of the Weber–Vögtle symbolism (cf. ref.<sup>6</sup>). Accordingly number denoting ring size is followed, in angular brackets, by appropriate symbols describing donor sites in the ring. Thus, e.g., for 18-crown-6 and for 18-monoazacrown-6 ethers we write 18 <O<sub>6</sub>> and 18 <NO<sub>5</sub>>, respectively. The IUPAC nomenclature of the investigated ligands is summarized in the Appendix part.

Bis(crowns) *IIIa–IIIc*

An appropriate bis(crown) *Ia–Ic* (1 mmol) was treated with a suspension of sodium hydride (0.05 g; 2 mmol) in dioxane (3 ml). Benzylbromide (0.22 g; 1.3 mmol) was added to the stirred mixture and kept under reflux for 8 h. The precipitated salts were separated by a filtration over a short column of silica and washed with chloroform. The solvents were taken down on aspirator and the product isolated by a column chromatography on alumina (Merck; act. II). Data are in Tables I and II.

TABLE I  
Mono- and bis(crown) compounds *II–V*

Compound	Yield %	B.p. °C/Pa	Eluent CHCl <sub>3</sub> : CH <sub>3</sub> OH	Formula (M.w.)	Calculated/Found		
					% C	% H	% N
<i>IIa</i>	59	165/10	—	C <sub>20</sub> H <sub>40</sub> N <sub>2</sub> O <sub>7</sub> (420.6)	57.11	9.59	6.60
					56.96	9.38	6.32
<i>IIb</i>	58	190/10	—	C <sub>24</sub> H <sub>48</sub> N <sub>2</sub> O <sub>9</sub> (508.6)	59.67	9.51	5.51
					56.48	9.42	5.40
<i>IIc</i>	52	—	100 : 0	C <sub>28</sub> H <sub>56</sub> N <sub>2</sub> O <sub>11</sub> (596.7)	56.36	9.46	4.70
					56.15	9.29	4.51
<i>IIIa</i>	93	—	100 : 1	C <sub>26</sub> H <sub>44</sub> N <sub>2</sub> O <sub>7</sub> (496.7)	62.88	8.93	5.64
					62.82	8.59	5.41
<i>IIIb</i>	71	—	50 : 1	C <sub>30</sub> H <sub>52</sub> N <sub>2</sub> O <sub>9</sub> (584.8)	61.62	8.96	4.79
					60.74	8.68	4.58
<i>IIIc</i>	76	—	50 : 1	C <sub>34</sub> H <sub>60</sub> N <sub>2</sub> O <sub>11</sub> (672.9)	60.69	8.99	4.16
					60.52	8.72	3.86
<i>IVa</i>	98	—	50 : 1	C <sub>19</sub> H <sub>38</sub> N <sub>2</sub> O <sub>6</sub> (390.5)	55.28	8.84	6.45
					55.82	9.21	6.48
<i>IVb</i>	60	—	25 : 1	C <sub>23</sub> H <sub>46</sub> N <sub>2</sub> O <sub>8</sub> (478.6)	55.15	8.87	5.37
					55.35	9.19	5.55
<i>IVc</i>	77	—	25 : 1	C <sub>27</sub> H <sub>54</sub> N <sub>2</sub> O <sub>10</sub> (566.7)	55.06	8.91	4.59
					55.04	9.02	4.30
<i>Va</i>	90	85/10	—	C <sub>11</sub> H <sub>23</sub> NO <sub>4</sub> (233.3)	56.63	9.94	6.00
					55.69	9.55	5.73
<i>Vb</i>	88	115/10	—	C <sub>13</sub> H <sub>27</sub> NO <sub>5</sub> (277.4)	56.29	9.81	5.05
					56.13	9.85	4.96
<i>Vc</i>	87	155/10	—	C <sub>15</sub> H <sub>31</sub> NO <sub>6</sub> (321.4)	56.05	9.72	4.36
					56.11	9.64	4.40

Bis(crowns) *IVa—IVc*

Prepared from appropriate monoazacrown ethers *VIIIa—VIIIc* and 1,3-bis(*p*-toluenesulphonyloxy)propane analogously as described above for the bis(crowns) *IIa—IIc*. The products were isolated by a column chromatography on alumina (Reanal; act. II). Data are in Tables I and II.

N-(2-Hydroxy-1-propyl)crowns *Va—Vc*

An appropriate monoazacrown ether *VIIIa—VIIIc* (4 mmol) was heated with an excess of methyloxirane (5 ml; 70 ml) in a heavy wall ampoule (120°C; 5 h). The product was isolated by a short-path distillation (Kugelrohr). Data are in Tables I and II.

## Potentiometric Measurements

Formation of sodium complexes was followed potentiometrically with sodium ion selective electrode (Radiometer G502) of 0.01M tetramethylammonium hydroxide in 99% aqueous methanol.

TABLE II

Mono- and bis(crown) compounds *II—V*: mass spectra

Compound	<i>m/z</i> (%)
<i>IIa</i>	420 ( $M^+$ , 0.1), 389 (39), 230 (34), 214 (100), 189 (80), 157 (18), 156 (15), 100 (30), 91 (45), 83 (23), 56 (40)
<i>IIb</i>	508 ( $M^+$ , 0.2), 477 (17), 276 (42), 258 (45), 246 (38), 232 (100), 100 (16), 85 (18), 83 (30), 56 (25), 45 (22)
<i>IIc</i>	596 ( $M^+$ , 0.5), 303 (25), 302 (100), 301 (16), 277 (24), 276 (98), 100 (24), 87 (11), 86 (13), 56 (42), 45 (54)
<i>IIIa</i>	308 (1), 230 (2), 214 (19), 188 (55), 100 (26), 91 (100), 56 (92), 45 (42), 42 (43)
<i>IIIb</i>	352 (3), 309 (5), 258 (13), 232 (32), 100 (18), 91 (100), 56 (95), 45 (53), 42 (47)
<i>IIIc</i>	393 (3), 302 (45), 276 (92), 186 (6), 114 (10), 100 (38), 91 (100), 56 (95), 45 (90)
<i>IVa</i>	390 ( $M^+$ , 15), 285 (16), 215 (34), 188 (100), 186 (50), 172 (30), 156 (31), 128 (34), 114 (35), 100 (69), 70 (78), 56 (91)
<i>IVb</i>	478 ( $M^+$ , 30), 329 (30), 315 (28), 259 (50), 232 (100), 128 (38), 70 (50)
<i>IVc</i>	566 ( $M^+$ , 9), 373 (17), 359 (21), 303 (21), 276 (100), 274 (45), 244 (22), 172 (23), 100 (47), 70 (74), 45 (70)
<i>Va</i>	235 ( $M^+$ , 5), 218 (8), 202 (9), 188 (100), 158 (14), 144 (8), 114 (13), 100 (45), 56 (45), 45 (52)
<i>Vb</i>	277 ( $M^+$ , 1), 262 (1), 232 (100), 202 (4), 144 (9), 114 (7), 100 (11), 56 (14), 45 (12)
<i>Vc</i>	321 ( $M^+$ , 1), 276 (100), 232 (8), 188 (4), 114 (3), 100 (11), 56 (12), 45 (13)

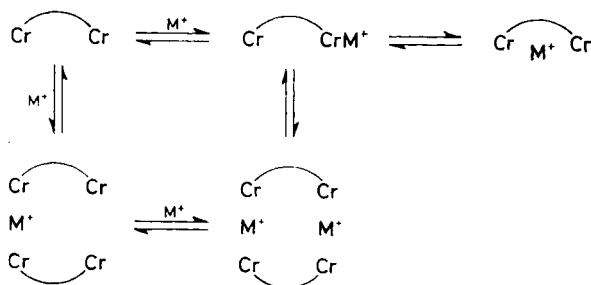
The free ligand ( $1 \cdot 10^{-3}$ – $1 \cdot 10^{-2}$ M solution) was titrated with  $1 \cdot 10^{-2}$ M sodium chloride solution (until about a fivefold excess was reached) using automatic titrator DTS 800 Radiometer, Copenhagen. The stability constants  $K_1$  for 1 : 1 sodium ion–ligand complex formation were calculated from the equation (1)

$$K_1 = (c_M - c_f) / [c_f(c_L - c_M + c_f)] \quad (1)$$

where  $c_M$  is the analytical concentration of the sodium ion,  $c_f$  is the concentration of the free (uncomplexed) form of the metal ion, and  $c_L$  is the analytical concentration of ligand. Titrimetric data obtained in the 0.2–0.8 region of  $c_M/c_L$  ratios were employed in the calculation. The average standard deviation was about 5%.

## RESULTS AND DISCUSSION

As it was pointed out already at earlier occasions, bis(crowns) may form with metal ions several complex species<sup>3,12,13</sup> differing in stoichiometry and/or in the spatial arrangement (Scheme 1).



SCHEME 1

In order to establish the main complex species arising from the bis(crowns) *Ia–If* in presence of sodium ion, we have made use of potentiometric titration with ion selective electrode. From the potentiometric data obtained upon gradual addition of sodium chloride to the ligand in 99% methanol (basified with  $1 \cdot 10^{-2}$ M tetramethylammonium hydroxide) we first evaluated stoichiometry of the dominant complex species in the solution making use of saturation curves. Next we calculated stability constants for the complex and compared the figures with those obtained in the corresponding mono- and bis(crown) subsidiary series.

### *Stoichiometry of the Dominant Complex Species in the Bis(crown) Series Ia–If*

Data from the potentiometric titration of the bis(crowns) *Ia–If* can be plotted as a function of the bound form of the metal ion ( $c_M - c_f$ ) vs the total (analytical)

metal ion concentration  $c_M$ . When the plot is arranged in a normalized form (i.e., divided by the analytical ligand concentration,  $c_L$ ), experimental curve describing a gradual ligand saturation by the metal ion is obtained.

The saturation curve plotted for the bis(crown) *Ib* in Fig. 1 shows that the ratio of the bound metal ion to the total ligand concentration,  $(c_M - c_f)/c_L$ , approaches rapidly to unity and then levels out demonstrating a prevalent formation of 1 : 1 complex in the solution. Entirely analogous situation found also for the other bis-(crowns) *Ia*, *Ic–If* strongly suggests that 1 : 1 complexes prevail generally in the investigated series.

The saturation curves do not differentiate\* between the monomeric and dimeric 1 : 1 complexes (cf. Scheme 1). Since, however, the corresponding equations for stability constants of the two alternative complexes are different (see Eqs (2) and (3))

$$K_1^{ML} = [ML]/[M^+][L] \quad (2)$$

$$K_1^{M_2L_2} = [M_2L_2]/[M^+]^2[L]^2 \quad (3)$$

distinction can be made between the two complexes by potentiometric titration at several ligand concentration. In this way, predominance of the monomeric species *ML* was invariantly found in the bis(crown) series *I*.

*Stability Constants for 1 : 1 Complexes: The Effect of Macroring Cooperation in Bis(crown) Sandwich Complex Formation*

The values of stability constants for 1 : 1 sodium ion–bis(crown) *Ia–If* complexes in methanol are summarized in Table III. The corresponding figures determined for the sodium ion complexes from the monocyclic ligands *Va–Vc* and *VIa–VIc* are summarized in Table IV. The monocyclic ligands represent, formally, building blocks for the bis(crown) compounds *Ia–If*.

A simple comparison of the corresponding values in Tables III and IV immediately suggests that a marked cooperation of both macrorings in the sodium ion–bis(crown) complex formation takes place. In order to quantify extent of the cooperation, we have introduced the coefficient of cooperation (Eq. (4))

$$\beta = K_1^B/K_1^M \quad (4)$$

where  $K_1^B$  is stability constant of a given sodium ion–bis(crown) complex and  $K_1^M$  is the corresponding value obtained for the sodium complex arising from an appropriate

\* Dimeric 1 : 1 complexes are usually ignored in a customary analysis. A surprisingly stable dimeric complex from a bis(benzocrown) has been however recently reported (ref.<sup>14</sup>).

monocyclic analogue. The coefficients  $\beta$  calculated for the bis(crowns) *Ia–If* are summarized in Table V.

As it follows from Table V, the values of the coefficients are always greater than unity ranging between about 2 and 20, in dependence on the macroring size and bis(crown) symmetry. The values of  $\beta$  decrease with the increasing macroring size being always significantly greater when both macrorings in the bis(crown) are the same.

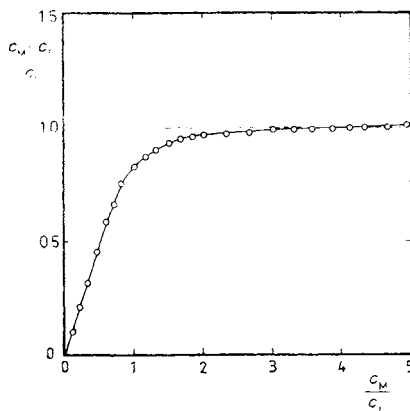
Although such a pattern of macroring cooperation agrees well with the concept of the intramolecular sandwich complex as visualized in Scheme 1, it might be argued that only a minor part of donor sites in one macroring participates, giving rise to a lariat complex<sup>15</sup> rather than to the sandwich formation.

TABLE III

The stability constants of 1 : 1 sodium ion complexes from bis(crowns) *Ia–If* in 99% methanol at 25°C

Formula	Ligand ACH <sub>2</sub> CH(OH)CH <sub>2</sub> B		$K_1 \cdot 10^{-3} \text{ (l mol}^{-1}\text{)}$
	A	B	
<i>Ia</i>	12 <NO <sub>3</sub> >	12 <NO <sub>3</sub> >	5.9
<i>Ib</i>	15 <NO <sub>4</sub> >	15 <NO <sub>4</sub> >	53.3
<i>Ic</i>	18 <NO <sub>5</sub> >	18 <NO <sub>5</sub> >	73.4
<i>Id</i>	12 <NO <sub>3</sub> >	15 <NO <sub>4</sub> >	27.5
<i>Ie</i>	12 <NO <sub>3</sub> >	18 <NO <sub>5</sub> >	69.9
<i>If</i>	15 <NO <sub>4</sub> >	18 <NO <sub>5</sub> >	46.2

FIG. 1  
Saturation of bis(crown) *Ib* with sodium ion  
in 99% methanol



In order to explore such an eventuality we have examined complexation properties of the "mini" analogues of bis(crown) compounds *VIIa–VIIc* in which one macroring moiety is replaced by a morpholine group. These compounds may serve as convenient models for assessing the lariat type of participation involving one nitrogen and one oxygen donor site. The stability constants of the sodium ion–ligand *VII* complexes are summarized in Table VI, together with the corresponding coefficients  $\beta$  calculated for the participation of the morpholine group.

TABLE IV

The stability constants of 1 : 1 sodium ion complexes from monocyclic ligands *Va–Vc* and *VIa–VIc* in 99% methanol at 25°C

Formula	Ligand A–R		$K_1 \cdot 10^{-3} \text{ (l mol}^{-1}\text{)}$
	A	R	
<i>Va</i>	12 $\langle \text{NO}_3 \rangle$	$-\text{CH}_2\text{CH(OH)CH}_3$	0.33
<i>VIa</i>	12 $\langle \text{NO}_3 \rangle$	$-\text{CH}_3$	0.11
<i>Vb</i>	15 $\langle \text{NO}_3 \rangle$	$-\text{CH}_2\text{CH(OH)CH}_3$	4.47
<i>VIb</i>	15 $\langle \text{NO}_3 \rangle$	$-\text{CH}_3$	2.57
<i>Vc</i>	18 $\langle \text{NO}_3 \rangle$	$-\text{CH}_2\text{CH(OH)CH}_3$	20.42
<i>VIc</i>	18 $\langle \text{NO}_3 \rangle$	$-\text{CH}_3$	6.10

TABLE V

The coefficients of macroring cooperation,  $\beta$ , in sodium ion complex formation from bis(crowns) *Ia–If*

Formula	Ligand $\text{ACH}_2\text{CH(OH)CH}_2\text{B}$		$\beta$
	A	B	
<i>Ia</i>	12 $\langle \text{NO}_3 \rangle$	12 $\langle \text{NO}_3 \rangle$	17.8 <sup>a</sup>
<i>Ib</i>	15 $\langle \text{NO}_4 \rangle$	15 $\langle \text{NO}_4 \rangle$	11.9 <sup>b</sup>
<i>Ic</i>	18 $\langle \text{NO}_5 \rangle$	18 $\langle \text{NO}_5 \rangle$	3.6 <sup>c</sup>
<i>Id</i>	12 $\langle \text{NO}_3 \rangle$	15 $\langle \text{NO}_4 \rangle$	6.2 <sup>d</sup>
<i>Ie</i>	12 $\langle \text{NO}_3 \rangle$	18 $\langle \text{NO}_5 \rangle$	3.4 <sup>e</sup>
<i>If</i>	15 $\langle \text{NO}_4 \rangle$	18 $\langle \text{NO}_5 \rangle$	2.2 <sup>f</sup>

<sup>a</sup>  $K_1^{\text{Ia}}/K_1^{\text{Va}}$ , <sup>b</sup>  $K_1^{\text{Ib}}/K_1^{\text{Vb}}$ , <sup>c</sup>  $K_1^{\text{Ic}}/K_1^{\text{Vc}}$ , <sup>d</sup>  $K_1^{\text{Id}}/K_1^{\text{Vb}}$ , <sup>e</sup>  $K_1^{\text{Ie}}/K_1^{\text{Vc}}$ , <sup>f</sup>  $K_1^{\text{If}}/K_1^{\text{Vc}}$ .



It is seen that the  $K_1$  as well as the  $\beta$  values for the morpholine derivatives *VIIa* to *VIIc* are markedly lower than those we found for the corresponding bis(crowns) *Ia–Ic*. It strongly suggests a more pronounced participation in the latter bis(crown) series, in accord with the concept of sandwich complexes.

*Effect of Hydroxyl Group at the Trimethylene Hinge on the Intramolecular Sandwich Complex Formation*

As it may be inferred from a comparison of the sodium complex stability data we obtained for the 2-hydroxypropyl and for the methylsubstituted azacrowns (*Va–Vc* and *VIa–VIc*, respectively) in Table IV, the lateral hydroxyl substituent in the monocyclic series participates rather weakly in the complex formation, the ratio of  $K_1^V/K_1^{VI}$  being about 2–3 irrespective of the size of macroring.

TABLE VI

The stability constants of 1 : 1 sodium ion complexes,  $K_1$ , from the "mini" bis(crowns) *VIIa–VIIc* in 99% methanol and the corresponding coefficients of cooperation,  $\beta$ , of the morpholine (Morph) group

Ligand ACH <sub>2</sub> CH(OH)CH <sub>2</sub> Morph		$K_1 \cdot 10^{-3}$ (l mol <sup>-1</sup> )	$\beta$
Formula	A		
<i>VIIa</i>	12 <NO <sub>3</sub> >	0.37	1.1 <sup>a</sup>
<i>VIIb</i>	15 <NO <sub>4</sub> >	5.65	1.3 <sup>b</sup>
<i>VIIc</i>	18 <NO <sub>5</sub> >	24.90	1.2 <sup>c</sup>

<sup>a</sup>  $K_1^{VIIa}/K_1^{Va}$ ; <sup>b</sup>  $K_1^{VIIb}/K_1^{Vb}$ ; <sup>c</sup>  $K_1^{VIIc}/K_1^{Vc}$ .

TABLE VII

The ratios of the stability constants for sodium ion complexes from the hydroxyl-substituted ( $X = OH$ ) and from the parent ( $X = H$ ) bis(crown) compounds ACH<sub>2</sub>CH(X)CH<sub>2</sub>A (*Ia–Ic* and *IVa–IVc*, respectively)

A	$K_1^I/K_1^{IV}$
12 <NO <sub>3</sub> >	0.67
15 <NO <sub>4</sub> >	19.4
18 <NO <sub>5</sub> >	13.1

In order to assess similarly the effect of the lateral hydroxyl substituent in the bis(crown) sandwich complex formation, we have compared sodium complex stabilities in the hydroxyl-substituted (*Ia–Ic*) and in the unsubstituted parent (*IVa–IVc*) series. The ratios of the corresponding stability constants from the two compared series,  $K_1^I/K_1^{IV}$ , are in Table VII.

A striking dependence on ring size is immediately apparent. For the smallest bis(crown) homologues (*Ia* and *IVa*) the ratio  $K_1^I/K_1^{IV}$  is very close to unity (in actual fact, less than unity) indicating a practical absence of the hydroxyl participation in the sandwich complex formation. Whereas, for the higher homologues (*Ib* and *IVb*, *Ic* and *IVc*) the  $K_1^I/K_1^{IV}$  values are 19 and 13, respectively, indicating a very

TABLE VIII

The effect of substituent X on stability of sodium ion complexes arising from the bis(crown) compounds  $\text{ACH}_2\text{CH(X)CH}_2\text{A}$  in 99% methanol at 25°C

Formula	A	X	$K_1 \cdot 10^{-3} (\text{l mol}^{-1})$
<i>Ia</i>	12 $\langle \text{NO}_3 \rangle$	OH	5.90
<i>IIa</i>	12 $\langle \text{NO}_3 \rangle$	OCH <sub>3</sub>	9.41
<i>IIIa</i>	12 $\langle \text{NO}_3 \rangle$	OCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	4.84
<i>IVa</i>	12 $\langle \text{NO}_3 \rangle$	H	8.82
<i>Ib</i>	15 $\langle \text{NO}_4 \rangle$	OH	53.30
<i>IIb</i>	15 $\langle \text{NO}_4 \rangle$	OCH <sub>3</sub>	5.89
<i>IIIb</i>	15 $\langle \text{NO}_4 \rangle$	OCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	2.08
<i>IVb</i>	15 $\langle \text{NO}_4 \rangle$	H	2.75
<i>Ic</i>	18 $\langle \text{NO}_5 \rangle$	OH	73.40
<i>IIc</i>	18 $\langle \text{NO}_5 \rangle$	OCH <sub>3</sub>	21.10
<i>IIIc</i>	18 $\langle \text{NO}_5 \rangle$	OCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	4.66
<i>IVc</i>	18 $\langle \text{NO}_5 \rangle$	H	5.62

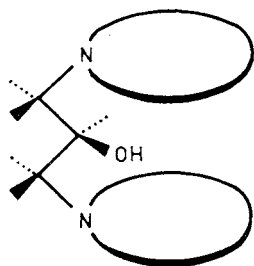


FIG. 2

The optimal arrangement of bis(crowns) *I* for sodium ion complexation

pronounced hydroxyl participation, much stronger than in the monocyclic series *Va* – *Vc* (cf. Table IV).

A simple rationale for this behaviour may be provided on the assumption that, in order to arrive at an effective participation, the hydroxyl group in the bis(crown) complex must protrude inside the central (interannular) cavity (Fig. 2). Examination of CPK models suggests that in the smallest bis(crown) *Ia* the protruding hydroxyl diminishes prohibitively the central cavity disallowing thus effective participation. In the larger bis(crown) homologues *Ib* and *Ic*, the diminution of the cavity is less stringent allowing enough space for an easy confinement of the sodium ion.

#### *Effect of Other Substituents at the Hinge on the Sandwich Complex Formation*

In order to get a broader insight into modus operandi of the lateral donor group participation in the bis(crown) sandwich complex formation, we have examined stabilities of sodium complexes from several bis(crown) series differing by the nature of substituent at the trimethylene hinge ( $X = \text{OH}, \text{OCH}_3, \text{OCH}_2\text{C}_6\text{H}_5$ ). Stability constants obtained in the comparative study are summarized in Table VIII.

Noteworthy, in particular, are the figures obtained for the higher homologues (*Ib*–*IVb*, *Ic*–*IVc*) revealing that hydroxyl participates much more effectively than the more basic methoxy or benzyloxy groups. In part, at least, the difference may be attributed to steric factors, the observed complex stability order  $\text{OH} > \text{OCH}_3 > \text{OCH}_2\text{C}_6\text{H}_5$  being in a qualitative accord with increasing steric demands of the participating group. However, also ability of the hydroxyl group to form intramolecular hydrogen bond with the nitrogen donor sites in the macrorings should be taken into consideration, since the hydrogen bonding may enhance considerably the electron-donating power<sup>16</sup> of the hydroxyl in coordinating the sodium ion.

#### APPENDIX

The IUPAC nomenclature of the ligands studied

- Ia*: 10,10'-(2-hydroxy-1,3-propanediyl)bis(1,4,7-trioxa-10-azacyclododecane)  
*Ib*: 13,13'-(2-hydroxy-1,3-propanediyl)bis(1,4,7,10-tetraoxa-13-azacyclopentadecane)  
*Ic*: 16,16'-(2-hydroxy-1,3-propanediyl)bis(1,4,7,10,13-pentaoxa-16-azacyclooctadecane)  
*Id*: 13-[2-hydroxy-3-(1,4,7-trioxa-10-azacyclododec-10-yl)propyl]-1,4,7,10-tetraoxa-13-azacyclopentadecane  
*Ie*: 13-[2-hydroxy-3-(1,4,7-trioxa-10-azacyclododec-10-yl)propyl]-1,4,7,10,13-pentaoxa-16-azacyclooctadecane  
*If*: 16-[2-hydroxy-3-(1,4,7,10-tetraoxa-13-azacyclopentadec-13-yl)propyl]-1,4,7,10,13-pentaoxa-16-azacyclooctadecane  
*Iia*: 10,10'-(2-methoxy-1,3-propanediyl)bis(1,4,7-trioxa-10-azacyclododecane)  
*Iib*: 13,13'-(2-methoxy-1,3-propanediyl)bis(1,4,7,10-tetraoxa-13-azacyclopentadecane)  
*Iic*: 16,16'-(2-methoxy-1,3-propanediyl)bis(1,4,7,10,13-pentaoxa-16-azacyclooctadecane)

- IIIa*: 10,10'-(2-benzyloxy-1,3-propanediyl)bis(1,4,7-trioxa-10-azacyclododecane)  
*IIIb*: 13,13'-(2-benzyloxy-1,3-propanediyl)bis(1,4,7,10-tetraoxa-13-azacyclopentadecane)  
*IIIc*: 16,16'-(2-benzyloxy-1,3-propanediyl)bis(1,4,7,10,13-pentaoxa-16-azacyclooctadecane)  
*IVa*: 10,10'-(1,3-propanediyl)bis(1,4,7-trioxa-10-azacyclododecane)  
*IVb*: 13,13'-(1,3-propanediyl)bis(1,4,7,10-tetraoxa-13-azacyclopentadecane)  
*IVc*: 16,16'-(1,3-propanediyl)bis(1,4,7,10,13-pentaoxa-16-azacyclooctadecane)  
*Va*: 10-(2-hydroxypropyl)-1,4,7-trioxa-10-azacyclododecane  
*Vb*: 13-(2-hydroxypropyl)-1,4,7,10-tetraoxa-13-azacyclopentadecane  
*Vc*: 16-(2-hydroxypropyl)-1,4,7,10,13-pentaoxa-16-azacyclooctadecane  
*VIa*: 10-methyl-1,4,7-trioxa-10-azacyclododecane  
*VIb*: 13-methyl-1,4,7,10-tetraoxa-13-azacyclopentadecane  
*VIc*: 16-methyl-1,4,7,10,13-pentaoxa-16-azacyclooctadecane  
*VIIa*: 10-[2-hydroxy-3-(morpholino)propyl]-1,4,7-trioxa-10-azacyclododecane  
*VIIb*: 13-[2-hydroxy-3-(morpholino)propyl]-1,4,7,10-tetraoxa-13-azacyclopentadecane  
*VIIc*: 16-[2-hydroxy-3-(morpholino)propyl]-1,4,7,10,13-pentaoxa-16-azacyclooctadecane.

## REFERENCES

- Bourgoin M., Wong K. H., Hui J. Y., Smid J.: *J. Am. Chem. Soc.* **97**, 3462 (1975).
- Kimura K., Tamura H., Tsuchida T., Shono T.: *Chem. Lett.* **1979**, 611.
- Kikukawa K., He G.-X., Abe A., Goto T., Arata R., Ikeda T., Wada F., Matsuda T.: *J. Chem. Soc., Perkin Trans. 2*, **1987**, 135.
- Kimura K., Sakamoto H., Koseki Y., Shono T.: *Chem. Lett.* **1985**, 1241.
- Sakamoto H., Kimura K., Koseki Y., Matsuo M., Shono T.: *J. Org. Chem.* **51**, 4974 (1986).
- Weber E., Vögtle F.: *Top. Curr. Chem.* **98**, 4 (1981).
- Bělohradský M., Holý P., Stibor I., Závada J.: *Collect. Czech. Chem. Commun.* **52**, 2961 (1987).
- Calverley M. J., Dale J.: *Acta Chem. Scand.*, **B 36**, 241 (1982).
- Maede M., Furuyoshi S., Nakatsuji Y., Okahara M.: *Bull. Chem. Soc. Jpn.* **56**, 212 (1983).
- Johnson M. R., Jones N. F., Sutherland I. O.: *J. Chem. Soc., Perkin Trans. 1*, **1985**, 1637.
- Johnson M. R., Sutherland I. O.: *J. Chem. Soc., Perkin Trans. 1*, **1979**, 357.
- Calverley M. J., Dale J.: *Chem. Commun.* **1981**, 684.
- Kimura K., Ishikawa A., Tamura H., Shono T.: *J. Chem. Soc., Perkin Trans. 2*, **1984**, 447.
- Linsten G., Wennerström O., Thulin B.: *Acta Chem. Scand.*, **B 40**, 545 (1986).
- Schultz R., White B. D., Dishong D. M., Arnold K. A., Gokel G. W.: *J. Am. Chem. Soc.* **107**, 6659 (1985).
- Gutman V.: *Chimia* **31**, 1 (1977).

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