

Methyl Substituted Macrocyclic 'Crown' Polyethers and their Complexation

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Received June 3, 1980

In an attempt to produce ligands selective for sodium a series of compounds having two methyl groups substituted in 15 or 18 membered cyclic polyethers have been synthesised. E.m.f. and NMR solution studies show that 1:1 species are present for both sodium and potassium with the 18 membered series, whereas 1:2 potassium:ligand and 1:1 sodium:ligand are the major species for the 15 membered rings. This is supported by the isolation of crystalline complexes.

Introduction

Macrocyclic polyether 'crown' compounds may form complexes with stoichiometry 1:2 cation:ligand if the cation is too large to fit into the cavity. Pedersen [1] reported the isolation of compounds of this stoichiometry for the 15-membered ring crowns with cations having radii greater than 1.3 Å, i.e. potassium, rubidium, caesium, barium and the ammonium ion. Subsequently this stoichiometry was also reported for thallium [2], for strontium [3] and, under forcing conditions, e.g. with tetraphenylborate or perchlorate anions, for sodium [4] and calcium [3]. It has also been reported for magnesium [5] and calcium [6] salts of nitrophenols or nitrobenzoic acids with benzo-15-crown-5. That the ratio is not in itself proof of a 1:2 sandwich complex was shown by the crystal structure analysis [6] of calcium(3,5-dinitrobenzoate)₂ (benzo-15-crown-5)₂-dihydrate in which one benzo-15-crown-5 is coordinated to calcium and the other solvated by water. Sandwich complexes with the cation approximately equidistant from all five oxygen atoms in each of two ligands have been found in the [potassium-(benzo-15-crown-5)₂]⁺ ion [7] and in the [barium-(15-crown-5)₂]²⁺ ion [8]. In two sodium complexes the entity [sodium(benzo-15-crown-5)₂]⁺ was established by crystal structure analysis [9], the metal being sandwiched between two molecules of ligand

and coordinated by some of the oxygen atoms of each ligand.

Only for rubidium and caesium ions were 1:2 complexes originally [1] isolated with the 18-membered ring dibenzo-18-crown-6. A derivative with four methyl groups substituted in the macrocyclic ring yielded a 1:2 complex with caesium thiocyanate [10] shown by crystal structure analysis [11] to be a sandwich with twelve oxygen atoms equidistant from the caesium ion.

Investigation in methanol solution by the e.m.f. method showed [12] that cyclohexyl-15-crown-5 gave 1:2, as well as 1:1 complexes with potassium and caesium. For caesium, four derivatives of 18-crown-6 were used [12]; dibenzo-18-crown-6 gave the largest formation constant for the 1:2 complex. The ratio of 1:1 and 1:2 complex formation is solvent dependent: in aqueous methanol evidence for 1:2 complex formation by a calorimetric method was obtained [13] only for methanol concentrations greater than 70% by weight. ¹³³Cs NMR measurements [14] in dimethyl sulphoxide or dimethyl formamide gave measurable values of K₂ for 18-crown-6, but not for dibenzo-18-crown-6. Proton NMR studies also indicated a 1:1 complex for sodium and a sandwich for potassium with benzo-15-crown-5 in methanol [15], and a fully separated 2:1 crown-ion pair has been observed between difluorenylbarium and benzo-15-crown-5 in tetrahydrofuran [16]. Where a sandwich complex has been found in the solid, the conformation adopted by the ligand is one in which the oxygen atoms are approximately coplanar and the aliphatic carbon atoms are all on one side of this plane, the cation being on the other. The difference between the conformation found for benzo-15-crown-5 in a 1:2 complex and the 1:1 sodium complex [7] resulted from a change of sign of two gauche torsion angles consistent with the two conformations having approximately equal energy. In sandwich complexes the benzene rings do not stack parallel as in some aromatic compounds, but are staggered, being related by a centre of symmetry in the potassium complex of benzo-15-crown-5 [7] and a four-fold inversion complex in the

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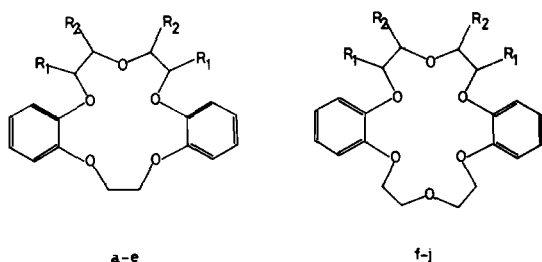


Fig. 1. Formulae and trivial names of the 15 (a-e) and 18 (f-j) membered cyclic polyethers

(a-e)		
$R_1 = R_2 = H$	dibenzo-15-crown-5	(a)
$R_1 = H, R_2 = CH_3$	7,9 <i>rac</i> -dimethyldibenzo-15-crown-5	(b)
	7,9 <i>meso</i> -dimethyldibenzo-15-crown-5	(c)
$R_1 = CH_3, R_2 = H$	6,10 <i>rac</i> -dimethyldibenzo-15-crown-5	(d)
	6,10 <i>meso</i> -dimethyldibenzo-15-crown-5	(e)
(f-j)		
$R_1 = R_2 = H$	dibenzo-18-crown-6	(f)
$R_1 = H, R_2 = CH_3$	7,9 <i>rac</i> -dimethyldibenzo-18-crown-6	(g)
	7,9 <i>meso</i> -dimethyldibenzo-18-crown-6	(h)
$R_1 = CH_3, R_2 = H$	6,10 <i>rac</i> -dimethyldibenzo-18-crown-6	(i)
	6,10 <i>meso</i> -dimethyldibenzo-18-crown-6	(j)

caesium complex with the racemate of tetramethyldibenzo-18-crown-6 [11].

In an endeavour to make complexes which would select for sodium and against potassium, we have designed molecules in which the conformation required for sandwich formation should be hindered. These are derivatives of 15-crown-5 rings substituted by two benzene rings and with further substitution of methyl groups in the macrocyclic ring. The formulae are shown in Fig. 1.

Experimental

Meso-6,10-Dimethyldibenzo[*b,h*]6,7,9,10,17,18-hexahydro-1,4,7,10,13-pentaoxacyclopentadecin (e)

A mixture of the diol I (Fig. 2) (11.1 g) and *meso*-bis(2-tosyloxypropyl)ether (18.5 g) in ethanol (300 ml) was heated until the solvent was refluxing and then treated with sodium hydroxide pellets (4.0 g) over a period of 20 min. The product after 16 h reaction was concentrated, poured into water and the brown oil obtained extracted with chloroform. After washing with water and reconcentration, the oil was dissolved in hot petroleum ether (b.p. 80–100°C) decolourised by treatment with charcoal, and again concentrated, to yield a pale brown oil (12.4 g). This oil, dissolved in hot methanol (100 ml), was treated with sodium perchlorate (10 g), and on cooling, the crystalline complex (9.7 g) m.p. 260°C separated. *Anal.* Found: C, 51.5; H, 5.2. Calcd. for $C_{20}H_{24}O_5 \cdot NaClO_4$: C, 51.5; H, 5.2%. Part of the sodium perchlorate complex (7.2 g) was suspended in a mixture of water (50 ml) and ethyl

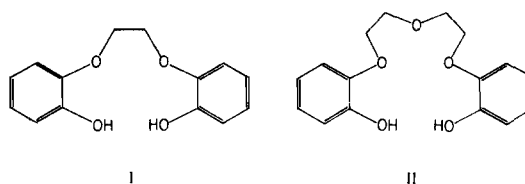


Fig. 2. Diols I and II.

acetate (25 ml) and heated under reflux for a short period. After cooling, the organic phase was separated, washed with water, and reconcentrated to yield a colourless oil which crystallised on cooling. Recrystallisation from petroleum ether (b.p. 80–100°C) yielded rosettes of the *meso* isomer. 3.9 g, m.p. 87°C. *Anal.* Found: C, 69.9; H, 7.1. Calcd. for $C_{20}H_{24}O_5$: C, 69.75; H, 7.0%; M.W. 344.4.

The following were similarly prepared: *rac*-7,9-dimethyldibenzo[*b,h*]6,7,9,10,17,18-hexahydro-1,4,7,10,13-pentaoxacyclopentadecin, (b), [yield 36%, m.p. 101°C. *Anal.* Found: C, 69.3; H, 7.05%; M.W. 338.5] from diol I and *rac*-bis(1-methyl-2-tosyloxyethyl)ether, and also *meso*-7,9-dimethyldibenzo[*b,h*]6,7,9,10,17,18-hexahydro-1,4,7,10,13-pentaoxacyclopentadecin (c) [yield 25%, m.p. 104°C. *Anal.* Found: C, 68.52; H, 6.99] from diol I and *meso*-bis(1-methyl-2-tosyloxyethyl)ether.

Rac-6,10-Dimethyldibenzo[*b,h*]6,7,9,10,17,18-hexahydro-1,4,7,10,13-pentaoxacyclopentadecin (d)

The diol I (4.8 g) and *rac*-bis-di(2-tosyloxypropyl)ether (12.3 g) in ethanol (200 ml) were treated with sodium hydroxide pellets (4.5 g) and heated under reflux for 18 h. The product was worked up in a way similar to that used for the *meso* isomer, but attempted crystallisation of the sodium perchlorate complex from methanol failed.

The crude oily material was extracted with petroleum ether (b.p. 100–120°C) 100 ml leaving a brownish tar. On cooling an oil was obtained which partially solidified; the solid material was collected, and recrystallised twice from methanol, yielding colourless needles (4.15 g) m.p. 87°C (*rapid heating*). *Anal.* Found: C, 69.5; H, 7.0%; M.W. 344.0. If the crystals were heated at a temperature just below the melting point for a short period, a crystalline modification occurred and a product m.p. 98°C was obtained.

Rac-7,9-Dimethyldibenzo[*b,k*]6,7,9,10,17,18,20,21-octahydro-1,4,7,10,13,16-hexaoxacyclooctadecin (g)

Rac-bis(1-methyl-2-tosyloxyethyl)ether (13.2 g), and the diol II (8.7 g) were refluxed with stirring in butanol (80 ml), and potassium hydroxide pellets (4.0 g) slowly added. Reflux was continued for 3 h, then the solution was cooled to room temperature and poured into water (150 ml). This was extracted

TABLE I. Log Association Constants in Methanol at 25 °C.^a

Compound	Potassium		Sodium
	K ₁	β ₂	K ₁
a	2.0	5.21	2.2
benzo-15-crown-5	2.8	5.95	3.05
15-crown-5	3.1	6.0	
b	1.4	4.57	1.9
c			2.1
d	0.9	4.0	1.1
e	1.4	4.67	1.5
18-crown-6	5.93(6.10)		(4.32)
benzo-18-crown-6	5.2		
f	4.8(5.00)		(4.36)
g	4.04		3.03
h	3.42		2.79
i	4.37		3.77
j	4.13		3.56

^aThe values quoted are logarithms of the constants $K_1 = [(M \cdot \text{crown})^+]/[M^+][\text{crown}]$ and $\beta_2 = [(M \cdot 2\text{crown})^+]/[M^+][\text{Crown}]^2$. Only significant digits are given. Values in parentheses from H. K. Frensdorff [12].

with chloroform (2 × 100 ml), and the combined organic layers washed with water (3 × 100 ml). The chloroform layer was decolourised with charcoal and concentrated to give a white solid, which was recrystallised from methanol to give needles, m.p. 112 °C (7.3 g, 63%). *Anal.* Found: C, 67.9; H, 7.3. Calcd. for C₂₂H₂₈O₆: C, 68.0; H, 7.3%.

The ligand may also be isolated as its calcium thiocyanate complex from the crude product obtained from the reaction mixture by dissolving in ethyl acetate and treating with excess calcium thiocyanate, when the complex readily precipitates. The free

ligand may then be obtained by boiling the calcium thiocyanate complex in water, extracting with chloroform, concentrating the chloroform layer, and recrystallising as before.

The following were similarly prepared: *meso*-7,9-dimethyldibenzo[b,k]-6,7,9,10,17,18,20,21-octahydro-1,4,7,10,13,16-hexaoxacyclooctadecin (h) m.p. 103–5 °C. [*Anal.* Found: C, 68.1; H, 7.25%] from diol II and *meso*-bis(1-methyl-2-tosyloxyethyl)ether, *rac*-6,10-dimethyldibenzo[b,k]-6,7,9,10,17,18,20,21-octahydro-1,4,7,10,13,16-hexaoxacyclooctadecin m.p. 80–1 °C. [*Anal.* Found: C, 68.25; H, 7.3%] from diol II and *rac*-bis(2-tosyloxypropyl)ether, and *meso*-6,10-dimethyldibenzo[b,k]-6,7,9,10,17,18,20,21-octahydro-1,4,7,10,13,16-hexaoxacyclooctadecin m.p. 103 °C [*Anal.* Found: C, 68.15; H, 7.2%; M.W. 390.1] from diol II and *meso*-bis(2-tosyloxypropyl)ether. The molecular weights found have been obtained from the density and X-ray measurements of unit cell dimensions.

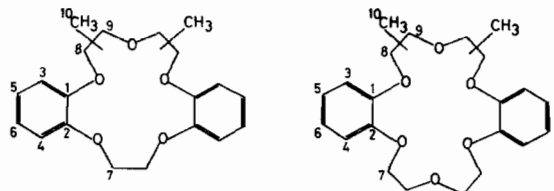
Measurement of Association Constants

Association constants, as previously described [17] were measured in Analar methanol at 25 °C by a potentiometric method using an ion selective electrode. Results are given in Table I. The reference electrode, making contact with the test solution by a porous plug, was a silver-silver chloride electrode in a saturated solution of sodium chloride in methanol. The ligand was added either as solid portions or by titration, and results were then calculated using the Miniquad program [18, 19]. Satisfactory Nernst response was obtained on calibration of the ion selective electrodes in the required range of concentrations.

TABLE II. Isolated Complexes of Salts with Crown Ethers.

Compound	Solvent	MP (°C)	Analyses (%)					
			Found			Calcd.		
			C	H	N	C	H	N
KClO ₄ · 2a · H ₂ O	methanol	115	54.73	5.45		54.78	5.36	
Ca(NCS) ₂ · a · H ₂ O	ethyl acetate	292–4	48.45	4.66	5.66	48.97	4.52	5.71
KSCN · 2b · ½H ₂ O	acetone	107–9	62.01	6.56	1.52	61.95	6.21	1.76
NaClO ₄ · b · H ₂ O	methanol		49.05	5.05		49.54	5.41	
NaClO ₄ · e	methanol	260	51.5	5.2		51.5	5.2	
NaSCN · e ^a	acetone	155–6	59.05	6.16	2.81	59.29	5.69	3.29
KSCN · 2e · ½H ₂ O	acetone	154	62.03	6.41	1.81	61.94	6.21	1.76
Ca(NCS) ₂ · e · 2H ₂ O	acetonitrile	>360	49.25	5.22	5.18	49.25	5.26	5.22
Ca(NCS) ₂ · j	ethyl acetate	dec. >250	52.82	5.31	5.13	52.93	5.18	5.14

^aDried *in vacuo* before analysis.

TABLE III. ^{13}C NMR Resonances in ppm from TMS in CDCl_3 .


Compound	C_1^{a}	C_2^{a}	C_3	C_4	C_5	C_6	C_7^{b}	$\text{C}_{7\text{a}}$	C_8^{b}	C_9^{b}	C_{10}
a	-149.7	-149.7	-116.4	-115.6	-122.0	-122.0	-68.4		-69.8	-70.4	
b	-149.6	-149.6	-117.2	-114.2	-122.2	-121.7	-69.5		-76.3	-71.3	-18.7
d	-150.5	-147.9	-118.9	-113.8	-122.6	-121.3	-67.4		-77.5	-74.5	-17.3
e	-149.8	-148.0	-118.1	-113.8	-122.0	-121.3	-66.9		-76.2	-75.4	-16.9
f	-149.0	-149.0	-114.0	-114.0	-121.4	-121.4	-69.0	-70.0			
g	-149.6	-149.0	-114.4	-113.9	-121.5	-121.2	-69.3	-70.4	-74.2	-73.1	-18.6
h	-149.1	-149.1	-114.6	-113.8	-121.5	-121.3	-69.0	-70.0	-74.0	-72.0	-18.3
i	-150.1	-148.0	-117.6	-114.6	-121.9	-121.4	-69.2	-70.1	-75.3	-75.0	-16.7
j	-150.0	-147.8	-117.5	-114.4	-121.8	-121.3	-69.0	-70.1	-75.0	-75.0	-16.7

^aDifferentiation between carbon atoms 1 and 2 has not been made and they have thus been arbitrarily numbered C_1 and C_2 (similarly with the pairs C_3 , C_4 and C_5 , C_6). ^bAssigned by off-resonance decoupling and selective proton decoupling.

Complexes with Alkali and Alkaline Earth Metals

Stoichiometric ratios of ligand and metal salt were heated in a suitable solvent to give a clear solution and then filtered. Crystallisation of the complex generally occurred on cooling or allowing the solution to evaporate slowly at room temperature, and the relevant data of those complexes thus obtained are given in Table II.

Infrared spectra were recorded as nujol mulls or potassium bromide discs on a Perkin Elmer 457 Grating Spectrophotometer. Melting points were determined on a Koffler hot stage melting point apparatus. Elemental analyses were determined at the Microanalytical Laboratory, University College London.

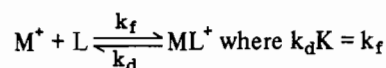
Measurement of NMR Spectra

^{13}C NMR data were obtained on a Jeol PS100 Fourier transform spectrometer using either CDCl_3 or $(\text{CD}_3)_2\text{CO}$ as solvent, and the deuterium of the solvent as lock. 8000 data points were used, and from 100 to 400 scans performed at a repetition time of 3 seconds. Where possible, peaks were assigned using off-resonance decoupling and selective proton decoupling. ^1H NMR spectra were determined on a Jeol PMX 60 spectrometer, and tetramethylsilane was used as internal reference for both ^{13}C and ^1H spectra. Spectra of the free ligands were entirely consistent with their proposed structures, and details are recorded in Table III.

Chemical shift variations due to changing metal ion concentration were obtained by adding the required molar quantities of freshly dried metal thiocyanate to 0.1 g of ligand, and dissolving in 0.5 ml of the deuterated solvent. The titration curves are illustrated in Fig. 3.

Results and discussion

The ion selective electrode titration curves obtained for the 18-crown-6 series show that only one species, namely ML, is formed from the interaction of metal and ligand. The values for potassium in Table I show that introduction of first one, then a second benzene ring lowers the complex formation constants of the resulting ligands and that substitution of hydrogen atoms by methyl groups in the heterocyclic ring reduces the formation constants by amounts which vary with the location of the methyl groups. With the exception of 18-crown-6 the rank order of the formation constants with sodium is the same as that with potassium. The value of K, the formation constant, depends upon the relative rates of the formation and decomplexation reactions



Several kinetic measurements of cyclic polyether complexation with alkali metals have indicated that

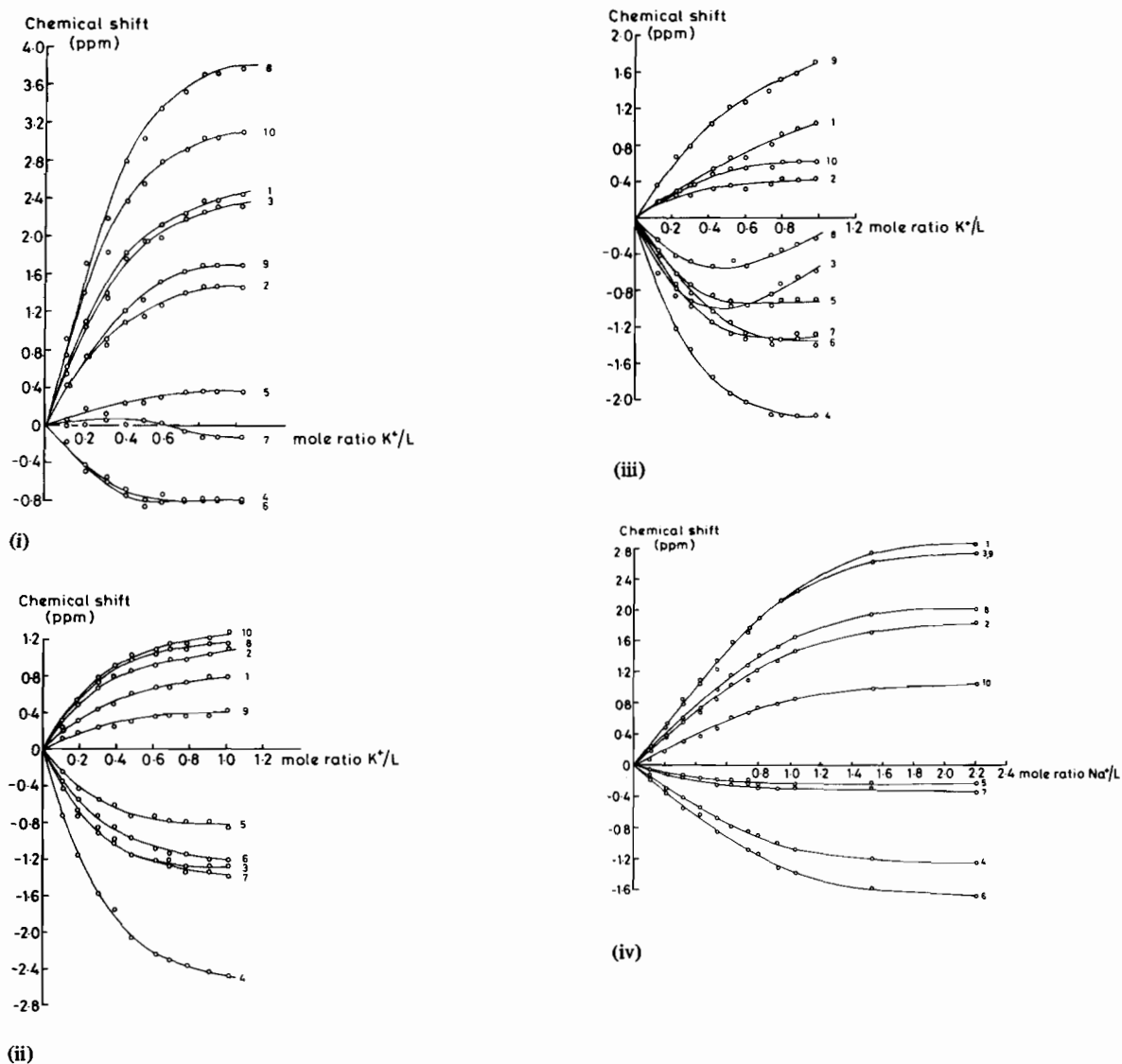


Fig. 3. Chemical shift changes in ppm on the addition of KSCN and NaSCN to crown in deuteroacetone. Positive values are shifts to higher field. i) 'b' with KSCN, ii) 'd' with KSCN, (iii) 'e' with KSCN, (iv) 'e' with NaSCN. Individual carbon atoms are numbered as in the diagram accompanying Table III.

the rate of decomplexation is an important factor in determining the stability of a complex, whereas rates of complexation are less variable [20-27].

If the present complexes behave in the same way, the compounds with more strained conformations in the complexed form would be expected to have faster rates of decomplexation and hence lower formation constants.

For the dibenzo derivatives [f-j] the conformation giving minimum average metal-oxygen distances is that having the six oxygen atoms coplanar with a central cation; the M-O distance 2.7 Å is larger than

the usual Na⁺...O nearest neighbour distances 2.3-2.5 Å so the greater ease of removal from sodium is as expected. The difference between the derivatives g-j can be understood qualitatively with the aid of space filling models. These suggest that substitution in the 7,9 position makes the conformation with all oxygen atoms planar very strained; in particular, 'h' appears less sterically crowded when the ring is considerably distorted from planarity.

Unsubstituted 18-crown-6 complexes of potassium have the six oxygen atoms coplanar with the cation in [28] or slightly out of [29] the plane,

depending upon the anion. By contrast the conformation of 18-crown-6 round sodium is quite different [28]; it occupies six out of seven positions in a pentagonal bipyramid and, although the average sodium-oxygen distance is shorter, 2.55 Å, this apparently favourable effect does not compensate for the more strained conformation of the ligand.

The e.m.f. titration curves for the 15 membered ring series show a 1:1 stoichiometry for sodium, but indicate that the dominant species for potassium is ML_2 , with little indication of the formation of ML . There is a small drop in stability constant in going from 15-crown-5 itself to benzo-15-crown-5. A much larger drop is observed on the introduction of a second benzene ring as in 'a', when molecular models indicate a much less flexible ring. Thus with sodium, it is difficult for the oxygen atoms to rearrange for good contact. In particular, when the two oxygens of the short OCH_2CH_2O bridge are facing inwards for bonding, then the pair of CH_2 hydrogens are fully eclipsed. For potassium, there is the added difficulty of steric interaction of the benzene rings when a sandwich is formed. For dibenzo-15-crown-5 the staggered arrangement found previously [7, 9, 11] is not compatible with good metal oxygen interactions. Further reduction in formation constants is observed for both sodium and potassium when methyl groups are introduced into the heterocyclic ring, but the hoped-for selectivity for sodium over potassium is not obtained. The crowding appears to be particularly severe for 'd', where molecular models show that a twisted conformation for the free ligand is favoured, and near planar oxygen conformations are severely strained.

The stoichiometry in solution has also been established by ^{13}C NMR titrations carried out in deuterioacetone. Figure 3 shows the changes of chemical shifts of individual carbon atoms as the mole ratio of metal increases. For sodium with ligand 'e', the greatest change in slope occurs around the 1:1 mole ratio, but for potassium this occurs at the 1:2 ratio (metal:ligand). There is no obvious indication of any 1:2 species between sodium and 'e'.

Further examination of the curves obtained for ligand 'e' shows that a different conformation of the polyether ring is adopted in the sodium complex from that in the potassium complex. On the addition of sodium, four peaks (4, 5, 6, 7) are deshielded and six are shielded. When potassium is added to a solution of the ligand then six peaks (3, 4, 5, 6, 7, 8) are deshielded until the 1:2 metal to ligand ratio is reached. As the metal concentration is now increased, the curves for carbon resonances 3 and 8 go through maxima and now start to become shielded (as in the sodium experiment), suggesting that the sodium conformation is becoming present in greater concentration. The major solution stoichiometries are confirmed by analysis of the crystalline com-

plexes isolated and shown in Table II. Sodium complexes are 1:1 and potassium 1:2 for the 15-membered rings.

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