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On the nature of the interaction between potassium ions and bis(crown ether) derivatives as revealed by low-temperature carbon-13 nuclear magnetic resonance spectroscopy †

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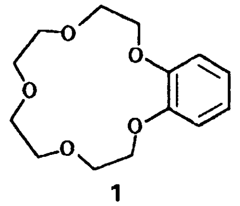
Bis(benzo-crown ether) derivatives linked by $HN(CH_2)_nNH$ chains where $n = 2$–6, 8 or 10 have been prepared and their interaction with potassium ions examined. In multinuclear NMR studies it was shown that the structure in solution was a rapidly exchanging series of several different complexes of 1 : 1 composition. Some of these exchange processes are characterised by NMR kinetics. A quantitative mass spectroscopic evaluation of the competition between pairs of bis(crowns) for a single cation (potassium, rubidium or caesium ion) was made. In ^1H, ^{13}C NMR and in FAB mass spectroscopic studies the crown where $n = 3$ in the series showed the most extreme behaviour, suggestive of stronger complexation and/or a different conformation.

Pedersen's crown sandwich hypothesis[1] was demonstrated with benzo-15-crown-5 (2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecine, **1**) for the first time in the crystal structure[2] and by NMR spectroscopy in solution.[3] The later concept of the 'clam' sandwich molecule (see type 1 in Scheme 1) formed from a sandwiching of alkali-metal cations between linked pairs of crown ethers was proposed by Bromels and Pedersen,[4] and developed by others subsequent to the discovery that the first bis(crown-5) compounds[5] could indeed sandwich potassium ions but would preferentially co-ordinate each face to a single sodium ion in donor solvents (type 2); many similar investigations followed.[6] A particular direction for bis(crown) research is exploitation of the K/Na selectivity in ion-selective electrodes.[6b–f] Crystal structures have been sparse for such bis(crown) complexes, but both type 1 (1 : 1) and 3 (2 : 2) sandwich structures have been demonstrated[7,8] by crystallography in the solid state. Structural information in solution is not definitive as to the state of aggregation of the complexes, although most interpretations considered only structure type 1. The solution, rather than the crystal, structure has importance for application in three-phase, ion-selective electrode and other membrane systems.[9] In this paper we argue from NMR evidence for the existence in solution of a multiplicity of exchanging structures. Competition between pairs of ligands for a slight deficit of alkali-metal cation has been monitored by FAB mass spectrometry.



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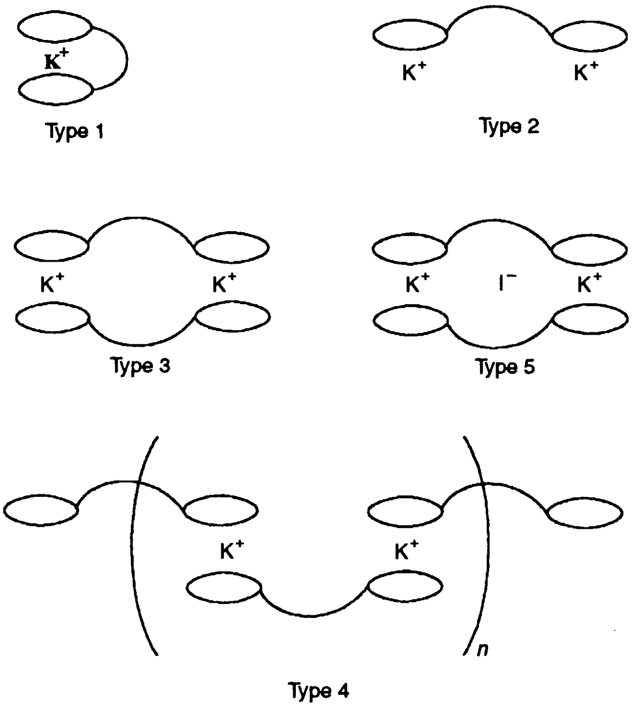

Scheme 1

Results and Discussion

It was necessary first to analyse the NMR spectra of individual compounds and to monitor the changes incurred on potassium-ion complexation. Subsequently, the behaviour of mixtures of free and complexed compound for several of the systems was analysed by variable-temperature ^{13}C NMR spectroscopy to investigate their kinetic behaviour.

The ^{13}C NMR spectra of the bis(benzo-15-crown-5) compounds **2**–**8** were monitored as mole fractions of KSCN were added. All spectra showed a major change in the movements of shift at a 1 : 1 potassium : crown ratio, this usually being the point of greatest shift change, as observed previously for related compounds.[9] As with the previous titrations,[9] the aromatic carbon signals separate into three pairs in terms of their behaviour. Again, the signals of the two carbons (a, f) connected to ether oxygens behave similarly to those of the other ether carbons, moving by 1.3–1.6 ppm. Although, in general, the two middle carbons (c, d) show opposite changes of shift, these movements are very small compared to the corresponding shifts in the NaSCN titrations.[9] Whilst the c/d pair of signals shows less sensitivity to potassium than to sodium, the b/e pair shows considerably more.

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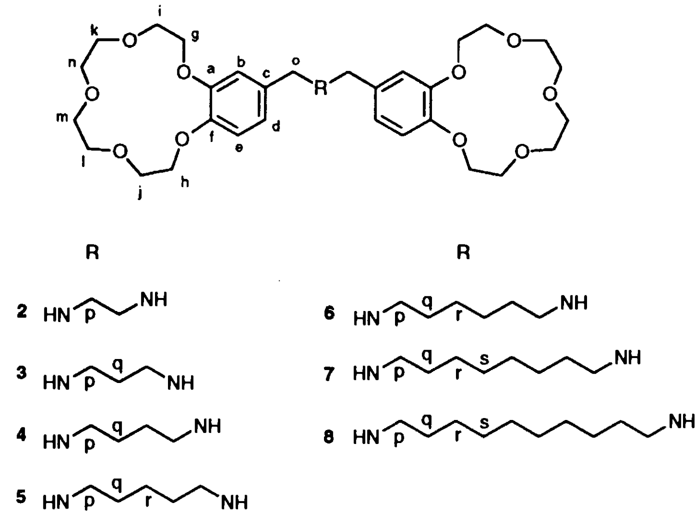
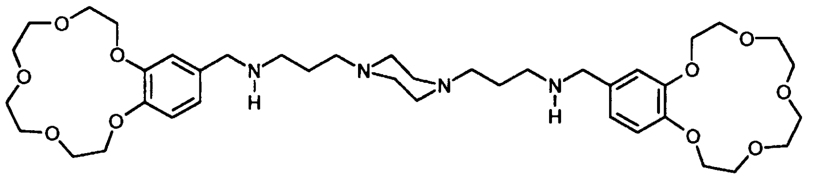
† *Non-SI unit employed:* cal = 4.184 J.





The linker carbons offered the greatest variety in their shift changes. For compounds **2**, **4** and **8** the greatest shift change was less than 0.2 ppm. Others (**6**, **7**) showed slightly more sensitivity though the greatest shift change was only ≈0.5 ppm. However, the NMR spectrum of the bis(crown) **5** contained two signals (q, r) which moved by more than +1.0 ppm. This must reveal a major change in environment caused by changes in conformation or the close proximity of another species. The strangest behaviour in any of the titrations is that of the linker section of **3** upon addition of KSCN (Fig. 1). Although the benzylic carbon (o) shows a typical shift change of $\approx +0.4$ ppm, the other two signals (p, q) show much greater changes. The signal of the second carbon attached to the amine nitrogen (p) moves by -2.5 ppm upon addition of 1 equivalent of KSCN, whilst that of the carbon at the centre of the propane bridge (q) moves by $+2.8$ ppm at the same point. These are the two largest shifts seen in any of the titrations. The shifts of the p and q carbon signals of several other bis(crowns) are also shown in Fig. 1. In the ^{1}H NMR spectra of the series the NH signals exhibited a high-frequency shift on addition of an equivalent of KSCN [shifts in ppm: 0.06 (**2**), 0.19 (**3**), 0.14 (**4**), 0.07 (**5**) and 0.06 (**6**)], again indicating **3** as the extreme.

All ^{13}C NMR titrations showed a major change at the 1 : 1 potassium : crown ratio which suggests relatively high formation constants since further addition of potassium does not significantly change the shifts. Presumably, therefore, some type of sandwich complex is being formed; unless the linker is too rigid or too short, there is no reason why this should not be of the type 1 ('clam') conformation rather than the type 3 ('double sandwich') since this should be preferred at this temperature and concentration. The shifts of the linker carbons of compound **5** may reflect some gamma-*gauche* effect, resultant on a conformational change upon complexation. Presumably this is not a problem for those bis(crowns) with longer and more flexible linker chains. There are a number of possible reasons for the extreme changes of shift of the linker carbons of **3**. It could be that this length of linker is the shortest possible to form a type 1 sandwich and that the linker methylenes are forced closer either to the enclosed potassium ion or to other parts of the molecule. This particular linker is potentially capable of internal hydrogen bonding between the two nitrogens; this may provide a reason for the extreme behaviour. Another alternative is the formation of a type 3 sandwich complex. Such an unusual conformation could explain the atypical behaviour of the linker carbons which would lie very close to the linker of the other sandwich. An argument against this explanation is the 'normal' behaviour of **2** which has an even shorter chain length. Its linker carbons show little change in shift which, in itself, could be explained by the formation of the type 3 sandwich. A further possibility could be the inclusion of an extra guest into the type 3 sandwich framework of the potassium complex of **3**, *e.g.* a solvent or more interestingly an anion which would certainly cause large shift changes. The alternation in behaviour between compounds with odd and even numbers of methylene groups has been noted before.[3]

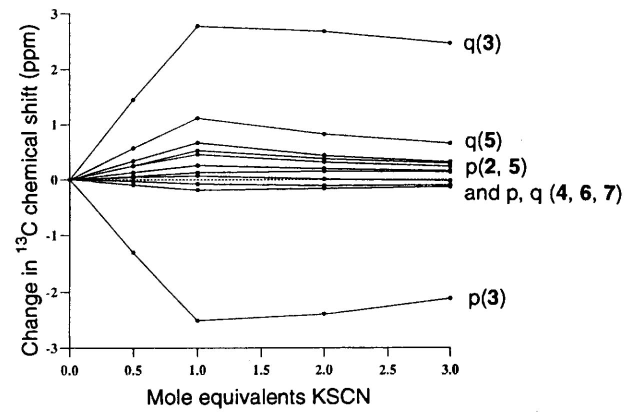


Fig. 1 Change in ^{13}C NMR chemical shift for specified linker carbons of compounds **2**–**7** on addition of KSCN

Compounds **3**, **8** and **9** were examined by ^{13}C variable-temperature NMR spectroscopy in the presence and absence of KI in deuteriated methanol (CD$_3$OD). The spectra give clear evidence for a ligand exchange such as in equation (1). Fig. 2(*a*)

$$\mathrm{L} + \mathrm{KL'} \rightleftharpoons \mathrm{KL} + \mathrm{L'} \qquad (1)$$

shows the spectrum for **3** with half an equivalent of KI at room temperature, Fig. 2(*b*) that at 215 K, and Fig. 2(*c*), that at 205 K. In the spectrum at room temperature the carbon signals

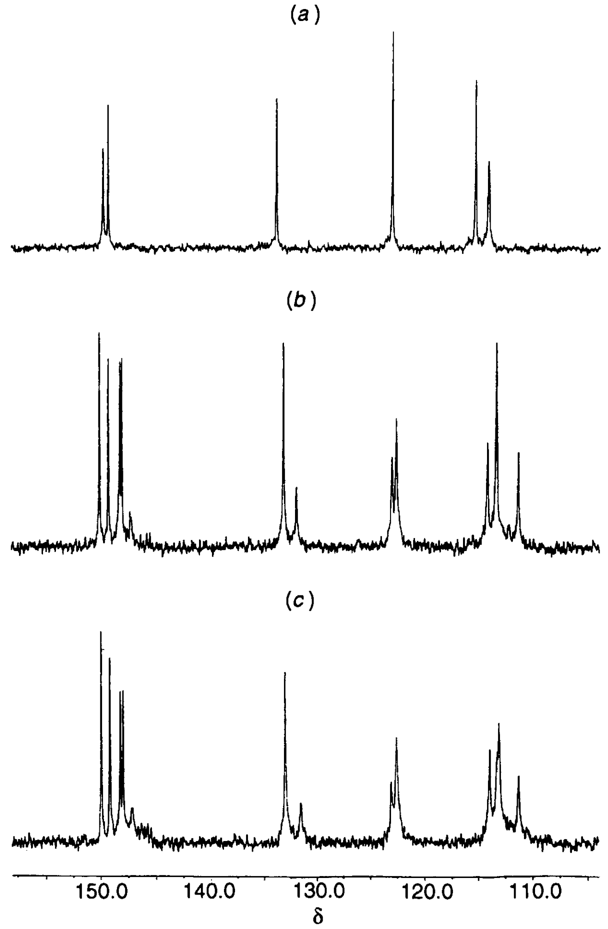


Fig. 2 The ^{13}C NMR spectra for compound **3** in CD_3OD solution with half an equivalent of KI at (*a*) 296, (*b*) 215 and (*c*) 205 K

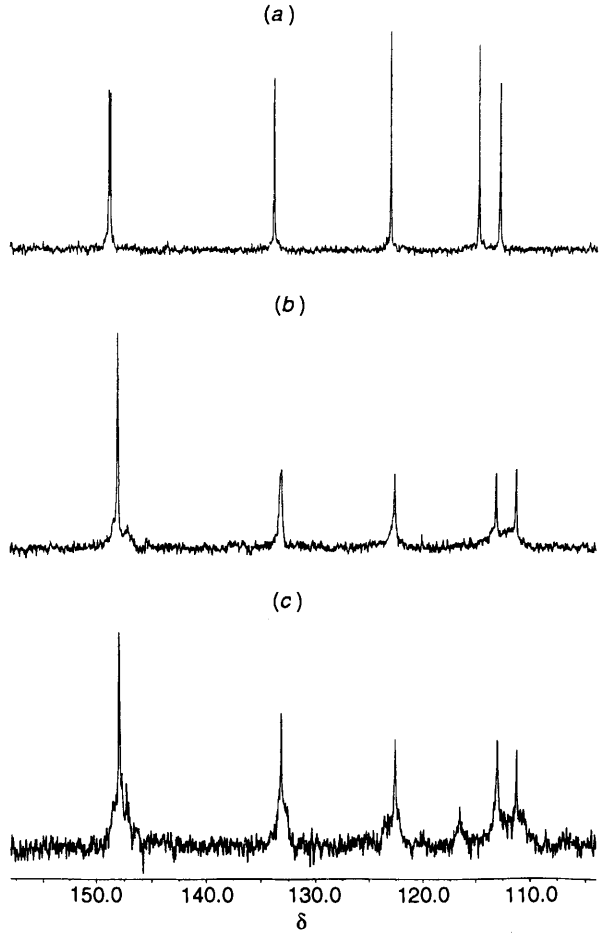


Fig. 3 The ^{13}C NMR spectra for compound **3** in CD_3OD solution with 1 equivalent of KI at 294, (*b*) 210 and (*c*) 200 K

represent averages; decoalescence (not shown) of individual signals occurs at temperatures from 270 K down. Several sharp separated signals occurring in pairs may be noted in Fig. 2(*b*) which apparently correspond to signals for free compound **3** and for its 1 : 1 complex. From the coalescence points of several of the pairs of signals values of $\Delta G^{\ddagger}$ were obtained, which correspond to the exchange processes shown in equation (1). The $\Delta G^{\ddagger}$ values (average 12.22 ± 0.07 kcal mol^{-1}) are in the range commonly found for the dissociation of alkali-metal cations from single or bis(crown) chelates (see Table 1).

Fig. 3 shows the spectra of a 1 : 1 mixture of KI and compound **3** at 294, 210 and 200 K. These spectra indicate the signals are undergoing a *further* exchange process, just beginning to slow at temperatures around 210 K. The separated signals do *not* occur in the region where the signals of free compound **3** appear, from which it may be deduced that no free **3** is present. Thus the process observed does not involve substantial quantities of free **3**. Disproportionation of a 1 : 1 complex to give complexes with one K per face (type 2) is ruled out, since the stoichiometry would have to comply with equation (2).

$$\text{type 1} \longrightarrow \text{type 2} + \text{free L} \qquad (2)$$

Slowing of conformational processes such as torsional movements was also ruled out as being much too rapid, based on earlier work with NMR spectroscopy and simulated molecular dynamics.[10] We conclude that the reaction mixture at these low temperatures contains entities essentially with a preserved 1 : 1 ratio of KI to compound **3** in a process of exchange probably faster than process (1). Possible identities of the species present include the 1 : 1 complex (Scheme 1, type 1), the 2 : 2 complex (Scheme 1, type 3) and higher oligomers (Scheme 1, type 4) which preserve the 1 : 1 ratio. The last two would be entropically favoured at low temperatures. However, we earlier demonstrated that chloride could be complexed to similar compounds in a unique site.[9] It is possible that iodide is incorporated here, acting as a bridge between crowns (*e.g.* type 5). Additional evidence favouring type 5, Scheme 1, was adduced from further spectra involving K : L ratios of 2 : 1 and 3.64 : 1. At higher ratios of K the temperature for decoalescence is higher, while at the lowest temperatures the separated signals are more discrete. Thus an excess of KI *decreases* the rate of exchange. In considering whether the K or the I is responsible for this effect, since single-face K (type 2 complex) is ruled out it seems possible that the additional effect observed stems from iodide acting as 'glue' either internally or externally at the two sites suggested in previous work.[9] Ionic strength effects on aggregating mixtures are not ruled out.

Table 1 Kinetic parameters derived for the exchange of compound **3** with K^+·**3** in CD_3OD

Carbon	Coalescence temperature/K	$\delta\nu_{240\,K}$/ Hz	k/s^{-1}	$\Delta G^{\ddagger}$/kcal mol^{-1}
a	263	146.4	325.2	12.3
f	255	92.1	204.5	12.2
c	253	70.9	155.7	12.9
d	243	20.4	45.3	12.3
b	253	84.5	187.8	12.1
e	265	182.6	405.7	12.3
o	247	30.9	68.7	12.3
q	270	361.5	803.1	12.2

More evidence may be deduced from the threshold temperature for the exchange, which, for this process, is lower

Table 2 Activation parameters for compounds **3**, **8** and **9** exchanging with their potassium complexes

Compound	$\Delta G^{\ddagger}$/kcal mol^{-1}	n	σ_n
3	12.22	8	0.07
8	11.57	5	0.34
9	10.94	5	0.11

Table 3 Potassium-39 NMR linewidth data

Compound **3**		Compound **9**	
T/K	$\delta\nu_{\frac{1}{2}}$/Hz	T/K	$\delta\nu_{\frac{1}{2}}$/Hz
297	102.8	301	231
280	98.4	280	538
260	138.3	260	567
240	133.9	240	560
220	188.0	220	672
200	395.0	200	574

Mixtures of KI (0.2 mol dm^{-3}) and crown (0.055 mol dm^{-3}) in methanol. The ^{39}K NMR spectra were run on Bruker WM300 WB spectrometer.

than that for ligand exchange between the free and 1 : 1 complexed species as in equation (1) and likely to correspond to lower $\Delta G^{\ddagger}$. The conformation of the type 3 1 : 1 chelate cannot rearrange to type 1, without prior dissociation, and similarly for rearrangement of type 3 to type 4 and *vice versa*. Formation of anion-linked species is unlikely to require such a high energy, providing a more plausible explanation.

Compounds **8** and **9** gave similar results ($\Delta G^{\ddagger}$ 11.57 ± 0.34, 10.94 ± 0.11 kcal mol^{-1} respectively for the coalescence temperatures) (see Table 2). The difference in activation energies is significant; assuming the complexes present in each system are of the same structural type, the data in Table 2 reflect the order of kinetic stability of the complexes formed. For these compounds at the 1 : 1 composition (L : K) analogous low-temperature exchange processes were also revealed, again indicating the presence of oligomeric species.

Variable-temperature potassium NMR spectroscopy

Sodium and potassium have nuclear spins of $\frac{3}{2}$ and hence are quadrupolar which means that their NMR relaxation properties are affected by the surroundings of the nucleus. In a highly symmetrical environment (*e.g.* in a solvated form) the nuclei undergo a slow relaxation and a sharp line is obtained in the NMR spectrum. Upon complexation (*e.g.* to a crown ether) the asymmetric electric field gradient results in faster quadrupolar relaxation leading to much broader linewidths.

To investigate the possible exchange between these two environments an excess of sodium or potassium has to be used to facilitate observations [equation (3)]. Assuming a dynamic

$$M^* + ML \rightleftharpoons M + M^*L \qquad (3)$$

equilibrium, then at high temperatures the above exchange is rapid on the NMR time-scale and an averaged signal will be seen. If the process is to be studied by NMR spectroscopy then at lower temperatures the exchange must slow sufficiently for the signals of the two forms to separate. At an intermediate temperature it may be possible to extract kinetic data. This was first carried out by Shchori *et al.*[11] who plotted ^{23}Na linewidths against $1/T$. For fully complexed and fully solvated sodium samples, straight lines were obtained (though separated by large linewidth values). For samples containing a mixture of complexed and free sodium a 'Z-curve' was obtained. At low temperatures the exchange between the two forms is slow enough for the signals to be separated though the linewidth for complexed sodium is too great to be distinguished from the baseline and hence the linewidth at low temperatures is similar to that found for solvated sodium. At much higher temperatures the exchange rate is now fast enough for the signal to represent an averaged value of the two forms. Between these two extremes the method of Shchori may be used to derive kinetic parameters for this exchange for a simple Z-curve.

Two variable-temperature ^{39}K NMR experiments were performed. The compounds used were **3** and **9** which were each dissolved in 3 cm^3 deuteriated methanol at a concentration of 0.055 mol dm^{-3} along with KI at a concentration of 0.2 mol dm^{-3}, these concentrations being chosen to optimise the ^{39}K NMR spectra. The linewidths were measured at a range of low temperatures (see Table 3) and the logarithms of these values plotted against the reciprocal of the temperature. The plots were not simple Z-curves and could, as proposed by McDonnell,[12] suggest a double exchange mechanism involving at least two forms of complexed potassium: this could be due to the potassium being complexed in either a type 1 or a type 2 structure. No kinetic data could be evaluated. The linewidth values for reaction of **3** were uniformly narrower than those in the other system, **9**, while the exchange region is shifted to higher temperatures (see Table 3). This would suggest that the environment of the complexed potassium ions is less asymmetrical for the system with **3** and that the rate of exchange between complexed and free potassium ions is slower than in the other system. Thus **3** produces a kinetically more stable complex with potassium ions under these conditions (*i.e.* in the presence of an excess of potassium) than does **9**.

FAB mass spectra of metal complexes

It is usually required for any quantitative analysis of mass spectra that the sensitivity of the instrument to relevant species should be known. Quantitative study of redistribution reactions by mass spectrometry was impeded by lack of knowledge of sensitivities and three methods were described[13–15] to obviate this. The most quantitative involved a calculation of a 'constant' K from ion-current ratios for the parent ions in a boron halide-scrambling reaction at several temperatures, together with a graphical determination of ΔH from these, assuming corresponding ratios of sensitivities were invariant with temperature.[13] Other semiquantitative work used an interpolative method to determine sensitivities for non-isolable heteroleptic arsenic halides based on determined sensitivities for homoleptic ones.[14] When, in 1983, Johnstone and Rose[16] found that the relative peak heights of crown ether complexes of metal salts correlated approximately with their concentrations in the matrix based on known stability constants, many workers used the same FAB mass spectral technique to study host–guest interactions, although attempts have seldom been made to render results quantitative in the absence of known sensitivities. Dearden and co-workers[17–19] have argued that results from FAB mass spectral studies of crown ether–metal complexes are ambiguous due to the uncertainty as to where the ions are formed, in the matrix, beam, *etc.* Langley *et al.*[20] have recently summarised much of the work on FAB mass spectrometry of crown ether–alkali-metal cation mixtures. They demonstrated that the relative intensities of $[M + \mathrm{H}]^+$ and $[M + \mathrm{metal}]^+$ ions were widely different when these were generated from equimolar mixtures of the ligand and its metal complex, counselling that much of the interpretation in the literature which ignored this fact should be accepted with caution. They also made the obvious points that variables such as the matrix and the anion can alter the direction of any underlying equilibrium. Our results will be discussed in relation to the foregoing, stressing the qualitative nature of our interpretation.

One-ligand systems. All mixtures containing an alkali salt (MA) and just one crown (L) (equimolar) gave similar mass spectra. All showed $[L + M]^+$ as the major peak where M is the alkali metal in question. No peak corresponding to $[L]^+$ or $[L + H]^+$ was evident, consistent with the observations of Langley *et al.* (although NMR spectra seemed to suggest that all the systems studied here have relatively high stability constants). Hardly any breakdown was seen in these three sets of spectra, although a consistent peak appeared corresponding to the alkali-metal adduct of the matrix compound, *i.e.* at *m*/*z* 192 ($[m\text{-}O_2NC_6H_4CH_2OH + K]^+$), 238 ($[m\text{-}O_2NC_6H_4CH_2OH + Rb]^+$) or 286 ($[m\text{-}O_2NC_6H_4CH_2OH + Cs]^+$). A very low-intensity peak attributable to $[L + M + MA]^+$ was seen in the mass spectra of **4** + KSCN, **5** + KSCN, **2** + RbI and **4** + RbI. A slightly more intense peak at *m*/*z* 1027 was seen along with one at *m*/*z* 467 in the mass spectrum of **5** + RbI. These may be due to the breakdown of a double sandwich $[L_2Rb_2I_2]$ into $[L + Rb + 280]^+$ (*m*/*z* 1027) and $[L - 280 + Rb]$ (*m*/*z* 467) where *m*/*z* 280 is a very common breakdown product (a benzo-crown-5 fragment with a deprotonated methylene attached).

Two-ligand systems. In general, in the mass spectra of mixtures containing a 2:1 ratio of crown to alkali-metal salt the intensities of $[L + H]^+$ species were very small, consistent with the observations of Langley *et al.* However, the surplus of free crown was confirmed in the presence of ligand breakdown patterns (noticeably the fragment of *m*/*z* 281) which are not apparent in the 1:1 systems. As a consequence of only the L + M peaks providing the viable sensitivity, only the relative intensities of the $[L + M]^+$ peaks were compared (which also excludes any $[L + M + MA]^+$ species). The competition investigated is between two equimolar compounds L (presumably similar in sensitivity) to provide $[L + M]^+$ species; while the sensitivities of the two $[L + M]^+$ complexes are likely to be similar for a single metal ion, it is not likely that they would be similar to those for $[L + H]^+$. Hence, the height of each $[L + M]^+$ peak was measured and the ratio of the two calculated. Results are shown in Table 4. It should be stressed that the sensitivities have been presumed to be similar for the series of complex ions of one alkali-metal cation, and that the ratios are only qualitative indicators of selectivity. For example the competition between compounds **3** and **5** for potassium results in peaks at *m*/*z* 673 ($[\mathbf{3} + K]^+$) and 701 ($[\mathbf{5} + K]^+$). Although there is a small peak at *m*/*z* 663 ($[\mathbf{5} + 1]^+$) the main sign of surplus ligand is seen with the benzo-crown fragment peak at *m*/*z* 281. The heights of the two $[L + K]^+$ peaks were measured and the ratio of $[\mathbf{3} + K]^+:[\mathbf{5} + K]^+$ is calculated to be 4.31:1 which is inserted into Table 4 along with the reciprocal ratio $[\mathbf{5} + K]^+:[\mathbf{3} + K]^+$ (= 0.23:1). By reading down each column it is possible to assess ligand preferences under these conditions for each metal ion, *e.g.* for the potassium competitions where L^2 is **5** the relative intensities of $[L^1 + K]^+$ are 0.89 (L^1 = **2**), 4.31 (L^1 = **3**), 3.11 (L^1 = **4**), 0.80 (L^1 = **7**) and 0.97:1 (L^1 = **8**).

Table 4 Ratio of heights of mass spectral peaks, $[L^1 + M]^+:[L^2 + M]^+$

L^1	M^+	L^2					
		2	**3**	**4**	**5**	**7**	**8**
2	K^+		0.21	0.36	0.89	1.13	1.19
	Rb^+		0.99	1.00	1.12	1.57	0.89
	Cs^+		0.27	0.26	0.76	0.93	1.35
3	K^+	4.80		2.17	4.31	—	—
	Rb^+	1.01		1.17	1.20	—	—
	Cs^+	3.70		0.83	2.50	—	—
4	K^+	3.00	0.46		3.11	—	—
	Rb^+	1.00	0.85		2.18	—	—
	Cs^+	3.89	1.20		2.20	—	—
5	K^+	1.08	0.23	0.32		1.26	1.03
	Rb^+	0.90	0.84	0.50		1.42	1.52
	Cs^+	1.32	0.40	0.45		0.69	2.00
7	K^+	0.88	—	—	0.80		—
	Rb^+	0.63	—	—	0.70		1.06
	Cs^+	1.07	—	—	1.28		0.61
8	K^+	0.84	—	—	0.97	—	
	Rb^+	1.12	—	—	0.66	0.95	
	Cs^+	0.74	—	—	0.50	1.64	

The FAB mass spectra with potassium show the order of ligand selectivity to be: **3** > **4** > **2** ≈ **5** ≈ **7** ≈ **8**. The spectra involving the other two metal ions lead to a more confusing set of preferences. Those with rubidium in particular seem to show no pattern of selectivity apart from the relatively low intensity of all $[\mathbf{5} + Rb]^+$ peaks. This may, in part, be due to the formation of a double sandwich as described previously. Aside from this, no major difference in the selectivity of any of the compounds can be seen. The spectra with caesium show the order of selectivity to be: **3** ≈ **4** > **5** ≈ **7** > **2** ≈ **8**. Again the differences between the 'poorer' ligands were small when compared with the differences between the 'better' ones. As with the potassium spectra, **3** and **4** easily outperform the other crowns though in this case there is no major difference between them.

A clear pattern of preferences is seen for two of the three sets of competitions. Leaving aside for a moment the ambiguity of the rubidium results, a preference for two of the compounds in the series, **3** and **5**, can be seen. The particular preference for **3** in

Table 5 Analytical details of bis(crowns)

Compound	Formula	M.p./°C	Analysis (%)* C	H	N
2	$C_{32}H_{48}N_2O_{10}$	Oil			
	$C_{32}H_{48}N_2O_{10}\cdot 2HCl$	118–120	54.9 (55.4)	7.4 (7.3)	4.0 (4.0)
3	$C_{33}H_{50}N_2O_{10}$	Oil			
	$C_{33}H_{50}N_2O_{10}\cdot 2HCl\cdot H_2O$	214–220	54.2 (54.6)	7.3 (7.5)	3.7 (3.9)
4	$C_{34}H_{52}N_2O_{10}\cdot H_2O$	80–82	61.5 (61.2)	7.9 (8.2)	4.1 (4.2)
5	$C_{35}H_{54}N_2O_{10}$	Oil			
6	$C_{36}H_{56}O_{10}\cdot 0.5H_2O$	73–74	62.9 (63.9)	8.5 (8.3)	4.1 (4.15)
7	$C_{38}H_{60}N_2O_{10}$	66–70	64.8 (64.8)	8.9 (8.5)	3.7 (4.0)
8	$C_{40}H_{64}N_2O_{10}\cdot H_2O$	72–75	64.2 (64.0)	8.55 (8.8)	4.0 (3.7)

* Calculated values in parentheses.

the potassium series of spectra ties in with the findings of the NMR titrations described earlier which showed **3** to be unusual in its behaviour. It is important, however, not to extrapolate too much from these qualitative results. As well as those signals which were detected with small intensities, there may well be other species in solution which are not detected. The variation of solvents and counter ions used will affect the balance between solvated and complexed forms of each cation.

Conclusion

Whilst the bis(crowns) **2**–**8** behaved in a qualititatively similar way in most of these investigations, **3** showed more extreme behaviour in several instances: (*a*) the NH protons exhibit the greatest shift on addition of potassium ions; (*b*) there are larger shift changes for crown ether and aromatic ^{13}C signals; (*c*) the linker signals p and q show exceptionally large shifts; (*d*) there is slower exchange between free and complexed states in solutions containing excess of **3** than for **9**; (*e*) there is slower exchange of potassium ions between free and complexed states in solutions of **3** containing an excess of potassium ions than for **9** and (*f*) potassium ions apparently prefer to complex **3** in competition with other bis(crowns) under the conditions of the FAB experiment. It seems likely that the conformation of the $K^+ \cdot 3$ complex is qualitatively different [based on observations (*a*)–(*c*)]. These studies together suggest the exchanges of **3** are slower because they require a decomplexation step in the reaction sequence [from observations (*d*)–(*f*)]. The linker in **3** is close to the optimum length proposed for potassium complexation from previous studies.[3,6] The work also makes clear that any potassium sandwich present is a composite of rapidly exchanging structures, including minimally the generally accepted types 1 and 3, but excluding type 2. Future discussion of bis(crown) chelates should avoid the assumption that the crystal structure of one bis(crown) complex defines what is present in solution for analogous complexes.

Table 6 Molecular ions in mass spectra of bis(crowns)

Compound	*m*/*z*	EI	FAB	Accurate mass	
				Calculated	Obtained
2	620	$[M]^+$	*	620.3309	620.3296
3	634	$[M]^+$	$[M + 1]^+$	634.3465	634.3490
4	648	$[M]^+$	*	648.3622	648.3608
5	662	$[M]^+$	*	662.3778	662.3825
6	676	*	$[M + 1]^+$	676.3935	
7	704	$[M]^+$	$[M + 1]^+$	704.4248	704.4272
8	732	$[M]^+$	$[M + 1]^+$	732.4561	*

* Analysis not obtained.

Experimental

Synthesis

The bis(crowns) were available[9] or were prepared by the method of Kinnear and co-workers.[9] Characterisation data are shown in Tables 5–8.

Compound 2. To a solution of the 14-formyl derivative of benzo-15-crown-5, (0.89 g, 3.0 mmol), ethane-1,2-diamine (0.09 g, 1.5 mmol) and concentrated acetic acid (98%, 0.6 g) in dichloroethane (12 cm^3) was added sodium triacetoxyhydroborate (1.14 g, 5.4 mmol). The resultant solution was stirred for 48 h at room temperature and then made basic with a saturated solution of sodium hydrogencarbonate. This aqueous solution was extracted with ethyl acetate (2 × 50 cm^3) to remove any unreacted crown prior to extraction with chloroform (3 × 70 cm^3). After checking the composition of the organic extracts (TLC), they were combined and concentrated *in vacuo* to afford compound **2** as a colourless syrup (0.65 g, 70%). A portion of this was dissolved in Pr^{i}OH and treated with concentrated hydrochloric acid. The heavy white precipitate which formed was filtered off and was shown to be the dihydrochloride of **2**.

Compound 3. The preparation from the 14-formyl derivative (0.89 g, 3.0 mmol), and propane-1,3-diamine (0.11 g, 1.5 mmol) carried out in a similar manner to the preparation of **2** gave **3** as a colourless syrup (0.55 g, 58%). A portion of this was dissolved in Pr^{i}OH and treated with concentrated hydrochloric acid. The heavy white precipitate which formed was filtered off and shown to be the dihydrochloride of **3**.

Compound 4. The preparation from the 14-formyl derivative (1.48 g, 5.0 mmol) and butane-1,4-diamine (0.22 g, 2.5 mmol) carried out in a similar manner to the preparation of **2** gave **4** as a colourless syrup which solidified on standing to a white solid (1.10 g, 68%).

Compound 5. The preparation from the 14-formyl derivative (0.89 g, 3.0 mmol) and pentane-1,5-diamine (0.15 g, 1.5 mmol) carried out in a similar manner to the preparation of **2** gave **5** as a colourless syrup (0.50 g, 50%).

Compound 6. The preparation from the 14-formyl derivative (1.48 g, 5.0 mmol) and hexane-1,6-diamine (0.28 g, 2.5 mmol)

Table 7 Proton NMR spectral data (δ, *J*/Hz) for bis(crowns) **2**–**8**

	2	**3**	**4**	**5**	**6**	**7**	**8**
Aromatic	6.79–6.74 (m, 6 H)	6.78–6.74 (m, 6 H)	6.83–6.77 (m, 6 H)	6.83–6.76 (m, 6 H)	6.87–6.81 (m, 6 H)	6.83–6.79 (m, 6 H)	6.85–6.79 (m, 6 H)
Crown ether	4.05–4.03 (m, 8 H) 3.85–3.81 (m, 8 H) 3.69 (s, 16 H)	4.07–4.03 (m, 8 H) 3.85–3.81 (m, 8 H) 3.69 (s, 16 H)	4.13–4.06 (m, 8 H) 3.89–3.84 (m, 8 H) 3.72 (s, 16 H)	4.14–4.08 (m, 8 H) 3.90–3.86 (m, 8 H) 3.73 (s, 16 H)	4.17–4.10 (m, 8 H) 3.93–3.88 (m, 8 H) 3.76 (s, 16 H)	4.14–4.07 (m, 8 H) 3.89–3.85 (m, 8 H) 3.73 (s, 16 H)	4.14–4.07 (m, 8 H) 3.90–3.86 (m, 8 H) 3.73 (s, 16 H)
$C_6H_3CH_2N$	3.62 (s, 4 H)	3.63 (s, 4 H)	3.66 (s, 4 H)	3.68 (s, 4 H)	3.70 (s, 4 H)	3.67 (s, 4 H)	3.68 (s, 4 H)
NCH_2CH_2	2.66 (s, 4 H)	2.61 (t, 4 H, *J* = 6.8)	2.58 (br t, 4 H)	2.57 (t, 4 H, *J* = 7.0)	2.59 (t, 4 H, *J* = 7.1)	2.56 (t, 4 H, *J* = 7.1)	2.57 (t, 4 H, *J* = 7.2)
NH	1.76 (br s, 3 H)	1.85 (br s, 3 H)	1.92 (br s, 2 H)	2.00 (br s, 4 H)	2.05 (br s, 4 H)	1.73 (br s, 3 H)	1.87 (br s, 4 H)
NCH_2CH_2	—	1.64 (pnt, 2 H, *J* = 6.8)	1.51 (br pnt, 4 H)	1.60–1.20 (br m, 4 H)	1.53–1.47 (br m, 4 H)	1.0–1.40 (br m, 4 H)	1.50–1.40 (br m, 4 H)
Remaining methylenes	—	—	—	1.60–1.20 (br m, 2 H)	1.35–1.25 (br m, 4 H)	1.26 (br s, 8 H)	1.24 (br s, 12 H)

Table 8 Carbon-13 NMR spectral data for bis(crowns) **2**–**8** (in $CDCl_3$)

	2	**3**	**4**	**5**
Aromatic	149.12, 148.04, 133.81, 120.85, 114.04, i14.04	149.18, 148.19, 133.01, 120.92, 114.12, 114.05	149.18, 148.11, 133.57, 120.88, 114.06, 114.06	149.18, 148.12, 133.63, 120.89, 114.10, 114.10
Crown ether	71.01, 71.01, 70.53, 70.53, 69.63, 69.63, 69.20, 68.96	71.05, 71.05, 70.53, 70.53, 69.65, 69.65, 69.19, 68.99	71.08, 71.08, 70.57, 70.57, 69.69, 69.69, 69.22, 69.02	71.09, 71.09, 70.57, 70.57, 69.70, 69.70, 69.24, 69.03
$C_6H_3\mathit{C}H_2N$	53.64	53.55	53.70	53.78
$N\mathit{C}H_2CH_2$	48.70	47.97	49.18	49.28
$NCH_2\mathit{C}H_2$	—	29.39	27.90	29.92
Remaining methylenes	—	—	—	25.15
	6*	**7***	**8**	
Aromatic	148.89, 147.67, 134.66, 120.47, 113.85, 113.85	148.97, 147.77, 134.58, 120.54, 113.93, 113.93	149.10, 148.15, 132.66, 121.06, 114.01, 113.75	
Crown ether	70.48, 70.48, 70.00, 69.97, 69.17, 69.14, 68.90, 68.64	70.54, 70.54, 70.04, 70.04, 69.23, 69.19, 68.96, 68.71	70.96, 70.96, 70.47, 70.47, 69.62, 69.62, 69.02, 69.02	
$C_6H_3\mathit{C}H_2N$	53.05	53.05	53.50	
$N\mathit{C}H_2CH_2$	48.86	48.90	49.13	
$NCH_2\mathit{C}H_2$	29.81	29.81	29.63	
Remaining methylenes	27.03	29.32, 27.12	29.44, 29.44, 27.31	

* In CD_3CN, 75 MHz.

Table 9 Salts and solvents used in mass spectral experiments

Alkali-metal ion (M^+)	Salt (MA)	Solvent
K^+	KSCN	Acetonitrile
Rb^+	RbI	Methanol
Cs^+	CsCl	Methanol

carried out in a similar manner to the preparation of **2** gave **6** as a colourless syrup which solidified on standing to a white solid (0.50 g, 32%).

Compound 7. The preparation from the 14-formyl derivative (1.49 g, 5.0 mmol) and octane-1,8-diamine (0.36 g, 2.5 mmol) carried out in a similar manner to the preparation of **2** gave **7** as a colourless syrup (1.10 g, 63%) which solidified on standing.

Compound 8. The preparation from the 14-formyl derivative (1.49 g, 5.0 mmol) and decane-1,10-diamine (0.43 g, 2.5 mmol) carried out in a similar manner to the preparation of **2**, gave **8** as a waxy solid (0.79 g, 43%).

NMR studies

The spectra were obtained on Bruker AC 200 (room temperature ^{13}C titrations) and WM300 WB spectrometers (two-dimensional, variable-temperature ^{13}C and ^{39}K studies). Solvents used were CD_3OD and mixtures of CD_3CN with CD_2Cl_2 according to the solubility at specific temperatures for concentration-dependent NMR studies of compounds **2**–**8** and KSCN.

In all the ^{13}C NMR titrations the crown concerned was dissolved in CD_3CN (3 cm^3) at a concentration of 0.08 mmol dm^{-3}. To this was added $\frac{1}{2}$, 1, 2 and 3 equivalents of either NaSCN or KSCN. At each stage of the titration a complete (δ 0–200) ^{13}C NMR spectrum was obtained using a Bruker WM300 WB spectrometer.

For the variable-temperature ^{13}C NMR studies, compounds **3**, **8** and **9** were dissolved in CD_3OD (3 cm^3) at a concentration of 0.055 mmol dm^{-3}. The change in solvent was necessary to allow temperatures as low as 200 K to be accessed. A change of salt from KSCN to KI was also necessary to aid solubility.

Mass spectrometry

Typically, a solution was made up containing one or two crowns with one of three salts each at a concentration of 1.7×10^{-2} mol dm^{-3}. A sample of each solution was then mixed with the matrix liquid, *m*-nitrobenzyl alcohol (MNBA). Details of the salts and solvents used are shown in Table 9. The FAB spectra were obtained on a Kratos M58 ORF instrument; operating conditions were accelerating voltage 4 kV, atom beam 8 kV with Xe bombarding atoms.

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