Complexation of Monovalent Metal Ions by Lariat Ethers in Non-aqueous Solvents

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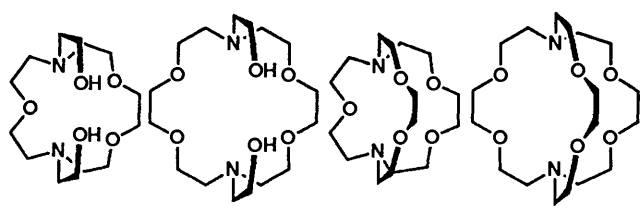
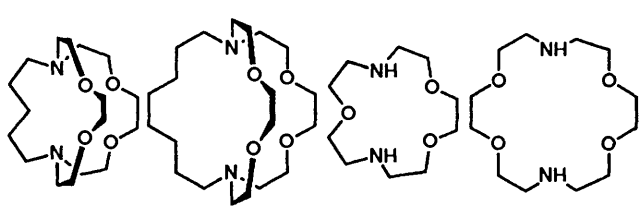
The stability constants (K) of 1 : 1 complexes of the lariat ethers 7,13-bis(2-hydroxyethyl)-1,4,10-trioxa-7,13-diazacyclopentadecane (L^1) and 7,16-bis(2-hydroxyethyl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (L^2) with monovalent metal ions have been determined by potentiometric titration in acetonitrile, methanol and dimethylformamide. Thus the complexes of Li^+, Na^+, K^+, Rb^+, Cs^+ and Ag^+ of L^1 and L^2 are characterized by $\log(K/dm^3\ mol^{-1})$ = 2.36 and 2.29, 3.93 and 3.65, 3.08 and 4.66, 2.50 and 3.56, 2.11 and 3.36, and 9.34 and 9.13, respectively, in dimethylformamide at 298.2 K. In some cases the rates of exchange of Li^+ and Na^+ in these complexes fall within the ^7Li and ^{23}Na NMR time-scale. This is exemplified by $[LiL^1]^+$ in dimethylformamide and methanol where the decomplexation of Li^+ is characterized by k_d (298.2 K) = 1.5 × 10^6 and 6.07 × 10^3 s^{-1}, $\Delta H_d^{\ddagger}$ = 65.4 and 27.1 kJ mol^{-1}, and $\Delta S_d^{\ddagger}$ = 92.9 and −81.5 J K^{-1} mol^{-1}, respectively, and by $[NaL^1]^+$ in acetonitrile and $[NaL^2]^+$ in methanol where the decomplexation of Na^+ is characterized by k_d (298.2 K) = 2.07 × 10^2 and 4.13 × 10^3 s^{-1}, $\Delta H_d^{\ddagger}$ = 52.6 and 42.8 kJ mol^{-1}, and $\Delta S_d^{\ddagger}$ = −24.1 and −32.0 J K^{-1} mol^{-1}, respectively. These data are compared with those for related systems.

The selective complexation of metal ions by crown ethers and cryptands is well established,[1–6] and is the genesis of the current interest in lariat ethers.[7–13] These are crown ethers to which one or more pendant arms are attached, and which appear to occupy a niche between the crown ethers and cryptands in their metal-ion complexation characteristics. A recurrent theme in studies of the chemistry of all three types of ligands has been their efficacy as membrane-transport agents for metal ions.[8,12,14] Thus, in addition to the selective complexation required in this role, the rates of complexation and decomplexation of metal ions are integral components of the overall rate of membrane transport quite apart from their own intrinsic interest. There are, however, few reports of kinetic studies of metal-ion complexation by lariat ethers.[13] Accordingly we have sought to extend the understanding of both the kinetic and equilibrium aspects of the lariat ethers and their monovalent metal-ion complexes through a study of 7,13-bis-(2-hydroxyethyl)-1,4,10-trioxa-7,13-diazacyclopentadecane, L^1, and 7,16-bis(2-hydroxethyl)-1,4,10,13-tetraoxa-7,16-diaza-cyclooctadecane, L^2,[9–11] which have the same number of oxygen- and nitrogen-donor atoms as the cryptands 4,7,13,-16,21-pentaoxa-1,10-diazabicyclo[8.8.5]tricosane, L^3, and 4,7,13,16,21,24-hexaaoxa-1,10-diazabicyclo[8.8.8]hexacosane, L^4,[15,16] respectively, and which, in the latter case at least, appear to co-ordinate alkali-metal ions with a similar disposition of donor atoms.[10,11] To extend current understanding of the complexation chemistry of L^1 and L^2, comparisons are made with that of L^3–L^8.





Experimental

Preparation of Materials.—Ligands L^1 and L^2 were prepared by methods similar to that in the literature.[9] Rubidium and caesium perchlorates were precipitated from solutions of their chlorides (BDH) by the addition of concentrated perchloric acid and were recrystallized from water until chloride was absent. Potassium perchlorate (BDH) was recrystallized from water. Lithium and sodium perchlorate (Fluka) and silver nitrate (Aldrich) were used as received after drying. All of the metal perchlorates were vacuum dried at 353–363 K for 48 h, and were then stored over P_2O_5 under vacuum.

Acetonitrile, dimethylformamide and methanol (BDH) were purified and dried by literature methods,[17] and were stored under nitrogen over Linde 3 Å molecular sieves in the cases of acetonitrile and methanol and over Linde 4 Å molecular sieves in the case of dimethylformamide, respectively. The water content of these solvents was below the Karl–Fischer detection level of approximately 50 ppm. Solutions of anhydrous metal perchlorates and L^1 or L^2 were prepared under dry nitrogen in a glove-box. For ^7Li and ^{23}Na NMR studies these solutions were degassed and sealed under vacuum in 5 mm NMR tubes which were coaxially mounted in 10 mm NMR tubes containing either D_2O, $(CD_3)_2CO$ or $(CD_3)_2SO$, which provided the deuterium lock signal.

Equilibrium Studies.—Apparent stability constants [equation (1)] for $[AgL^1]^+$ and $[AgL^2]^+$ were determined by duplicated

$$K = [ML^{n+}]/[M^+][L^n] \quad (1)$$

Table 1 Apparent stability constants for the complexation of monovalent metal ions by L" in dimethylformamide at 298.2 K

	log(K/dm^3 mol^{-1})							
M^+	$[ML^1]^+$ [a]	$[ML^2]^+$ [a]	$[ML^3]^+$ [b]	$[ML^4]^+$ [b]	$[ML^5]^+$	$[ML^6]^+$ [c]	$[ML^7]^+$ [d]	$[ML^8]^+$
Li^+	2.36 ± 0.03	2.29 ± 0.04	3.58		2.21 [e]	1.9		~0 [f]
Na^+	3.93 ± 0.01	3.65 ± 0.03	7.93	6.17	3.66 [g]	2.3	2.1	< 2 [h]
K^+	3.08 ± 0.01	4.66 ± 0.01	6.66	7.98	3.85 [e]	2.6		< 2 [h]
Rb^+	2.50 ± 0.03	3.56 ± 0.01	5.35	6.78	3.82 [e]	2.2		
Cs^+	2.11 ± 0.06	3.36 ± 0.01	3.61	2.16	2.90 [e]	2.0		0.61 [f]
Ag^+	9.34 ± 0.01	9.13 ± 0.09	12.41	10.07	9.40 [e]	7.7		9.91 [f]

[a] This work. [b] Ref. 20. [c] Ref. 23. [d] Ref. 24. [e] Ref. 22. [f] Ref. 25. [g] Ref. 21. [h] Ref. 26.

potentiometric titrations of 10^{-3} mol dm^{-3} $AgNO_3$ solution (20 cm^3) with 10^{-2} mol dm^{-3} L^1 or L^2 solution. The apparent stability constants of the analogues of Li^+, K^+, Rb^+ and Cs^+ were determined through duplicate competitive potentiometric titrations of 5.00 × 10^{-4} mol dm^{-3} $AgNO_3$ solution (20 cm^3) with a solution 2.50 × 10^{-2} mol dm^{-3} in the appropriate alkali-metal-ion perchlorate and 5.00 × 10^{-3} mol dm^{-3} of L^1 or L^2 as described in the literature.[18] Titrations were carried out under dry nitrogen in a thermostatted (298.2 ± 0.1 K) titration vessel connected to a thermostatted reference vessel by a salt bridge using silver-wire titration and reference electrodes. For a given experiment the titration and reference vessels and the salt bridge contained solutions made up in the same solvent with the reference solution being 10^{-2} mol dm^{-3} in $AgNO_3$. All titration solutions, and that in the salt bridge when used, were 5.00 × 10^{-2} mol dm^{-3} in NEt_4ClO_4. The apparent stability constants of $[NaL^1]^+$ and $[NaL^2]^+$ were determined through duplicate potentiometric titrations of 1.00 × 10^{-3} mol dm^{-3} $NaClO_4$ solution (20 cm^3) with 1.00 × 10^{-2} mol dm^{-3} L^1 and L^2 solutions, respectively, using an experimental system similar to that described above except that the silver-wire titration electrode was replaced by a Radiometer G502 Na^+-specific electrode. The stability constant of $[LiL^1]^+$ in acetonitrile was also determined using the Na^+-specific electrode which, although *ca.* 0.01 as sensitive to $[Li^+]$ as to $[Na^+]$, yielded highly reproducible results. An Orion Research SA 720 digital analyser was used to measure changes in potential for all titrations.

NMR Kinetic Studies.—The ^7Li and ^{23}Na NMR spectra were run at 116.59 and 79.39 MHz, respectively, on a Bruker CXP-300 spectrometer. In the ^7Li experiments 1000–6000 transients were accumulated in a 8192 data-point base over a 1199 Hz spectral width for each solution prior to Fourier transformation, and in the ^{23}Na experiments 1000–6000 transients were accumulated in a 2048 data-point base over a 8064 Hz spectral width for each solution. The solution temperatures were controlled to within ±0.3 K using a Bruker B-VT 1000 temperature controller. The Fourier-transformed spectra were subjected to complete lineshape analysis[19] on a VAX 11-780 computer to obtain kinetic data. The temperature-dependent ^7Li and ^{23}Na linewidths and chemical shifts employed in the lineshape analysis were obtained from a combination of extrapolation from low temperatures where no exchange-induced modification occurred and the linewidth and chemical shift variations of separate solutions containing either Li^+, $[LiL^1]^+$, $[LiL^2]^+$, Na^+, $[NaL^1]^+$ or $[NaL^2]^+$ as the only species.

Results and Discussion

Stability Constant Studies.—The apparent stability constants, K, of $[ML^1]^+$ and $[ML^2]^+$ in dimethylformamide at 298.2 K vary with M^+ in the sequences $Li^+ < Na^+ > K^+ > Rb^+ > Cs^+$ and $Li^+ < Na^+ < K^+ > Rb^+ > Cs^+$, respectively, and for both L^1 and L^2 the stability of the silver complex is much greater than that of the alkali-metal-ion complexes (Table 1). These are the same selectivity patterns as shown for the alkali-metal ions by the cryptands L^3 and L^4,[20] respectively, but the stabilities of the complexes formed by L^1 and L^2 including those of Ag^+ are less (except for $[CsL^2]^+$). The cryptands L^5 and L^6 possess cavities of similar size to those of L^3 and L^4, respectively, and have one and two less oxygen-donor atoms than these respective cryptands. This results in the stabilities of $[ML^5]^+$ varying with M^+ in the sequence $Li^+ < Na^+ < K^+ \approx Rb^+ > Cs^+$ and being substantially smaller than those of their $[ML^3]^+$ analogues, while $[ML^6]^+$ is characterized by yet lower stabilities with a maximum value for $[KL^6]^+$.[21–23] These trends are now examined in detail.

In the solid state the metal ions in $[NaL^2]^+$ and $[KL^2]^+$ are co-ordinated by two nitrogens and all six oxygens with both hydroxyl groups on the same side of the ring (the *syn* conformation)[10,11] so that the arrangement of donor atoms around the metal ions is similar to that observed in the solid state in the *inclusive* cryptate, $[KL^4]^+$.[16] The approximately spherical cavity of L^4 has a radius of *ca.* 1.4 Å[1–3] which compares with the eight-co-ordinate radii of 0.92, 1.18, 1.51, 1.61 and 1.74 Å for Li^+, Na^+, K^+, Rb^+ and Cs^+, respectively.[27] Thus K^+ has a close to optimum fit to the L^4 cavity while Li^+ and Na^+ are too small, and Rb^+ and Cs^+ are too large, and as a consequence $[KL^4]^+$ is the most stable of the alkali-metal-ion cryptates of L^4 in solution (Table 1). A similar rationale suggests that L^2 is capable of forming a cavity of *ca.* 1.4 Å radius in $[KL^2]^+$ in the *syn* conformation and that this complex is the least strained and, as a consequence, the most stable of the alkali-metal $[ML^2]^+$ complexes. However, the decrease in stability observed for $[ML^2]^+$ by comparison with $[ML^4]^+$ for the alkali-metal ions (except Cs^+) and Ag^+ indicates that solvent can better compete with the more flexible L^2 than with L^4 and that the ratio of the rate of decomplexation to that of complexation is smaller for the first species as is discussed in more detail below.

The cavity of L^3 is estimated to have a radius of *ca.* 1.1 Å.[1–3] This compares with the six-co-ordinate radii of 0.76, 1.02 (1.12), 1.38 (1.46), 1.52 (1.56) and 1.67 Å for Li^+, Na^+, K^+, Rb^+ and Cs^+,[27] respectively, so that Na^+ has a close to optimum fit to the L^3 cavity and forms an *inclusive* $[ML^3]^+$ cryptate,[15] while Li^+ is too small and K^+, Rb^+ and Cs^+ are too large. (Ideally the seven-co-ordinate radii should be used for comparison, but they are not available for all of the alkali-metal ions except where given in parentheses.) As a consequence, $[NaL^3]^+$ is the most stable of the alkali-metal cryptates of L^3 in solution as seen from Table 1. The observation that $[NaL^1]^+$ is the most stable of the alkali-metal $[ML^1]^+$ in dimethylformamide suggests that L^1 forms a cavity of *ca.* 1.1 Å radius in $[NaL^1]^+$ if it adopts the *syn* conformation. (There appear to be no reported solid-state structures of $[ML^1]^+$.) Nevertheless, the alkali-metal $[ML^1]^+$ complexes are significantly less stable than their cryptate $[ML^3]^+$ analogues, presumably because of the greater flexibility of L^1.

It is also seen from Table 1 that the decrease in the number of oxygen-donor atoms in L^5 and L^6 (which have the same cavity

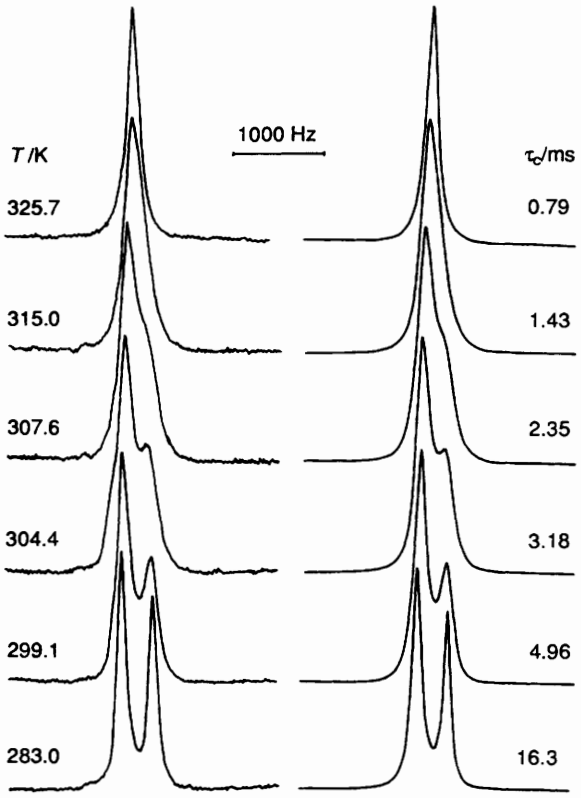


Fig. 1 Typical exchange-modified 79.39 MHz ^{23}Na NMR spectra of an acetonitrile solution of solvated Na^+ (0.0383 mol dm^{-3}) and $[NaL^1]^+$ (0.0625 mol dm^{-3}). Experimental temperatures and spectra appear to the left, and the best-fit calculated lineshapes and corresponding τ_c values to the right. The resonance of $[NaL^1]^+$ appears downfield from that of solvated Na^+

radii as L^3 and L^4, respectively) by one and two by comparison with L^3 and L^4, respectively, decreases the stabilities of the $[ML^5]^+$ and $[ML^6]^+$ complexes to values less than those characterizing $[ML^1]^+$ and $[ML^2]^+$ when $M^+ = Li^+$, Na^+ and K^+ (except in the case of $[KL^1]^+$ and $[KL^5]^+$). This illustrates the destabilizing effect of decreasing the number of donor atoms while retaining the relatively rigid cryptand structure in the cases of L^5 and L^6, and of retaining the same number of donor atoms while increasing flexibility in the case of L^1 and L^2. However, when M^+ becomes substantially larger than the cavities formed by these ligands, these correlations become less distinct, particularly in the case of Cs^+ for which the stabilities of the complexes become similar. The available data indicate that the diaza crown ethers, L^7 and L^8,[24–26,28] from which L^1 and L^2 may be derived through the substitution of hydroxyethyl groups at each nitrogen, do not produce complexes of comparable stability to those of L^1 and L^2, other than for Ag^+.

The stabilities of $[AgL^n]^+$ (Table 1) are substantially greater than those of their alkali-metal analogues as a consequence of the strong affinity of the soft acid[29,30] Ag^+ for the two amine nitrogens.[31,32] {The particularly high stability of $[AgL^3]^+$ may be a consequence of Ag^+ (r = 1.22 Å)[27] approximating to the cavity size of L^3.} However, this affinity results in a decrease in stability when the solvent is also a nitrogen donor and competes more effectively for Ag^+ as is indicated by the log(K/dm^3 mol^{-1}) values for $[AgL^1]^+$ in dimethylformamide, methanol and acetonitrile which are 9.34 ± 0.01, 9.36 ± 0.3 and 6.24 ± 0.1, respectively.

The log(K/dm^3 mol^{-1}) values for $[LiL^1]^+$ in methanol and acetonitrile are 2.85 ± 0.05 and 8.61 ± 0.02, respectively, and the analogous values for $[NaL^1]^+$ are 4.71 ± 0.01 and 7.00 ± 0.01, respectively, consistent with solvent competition with L^1 for Li^+ and Na^+ increasing in the sequence: acetonitrile < methanol < dimethylformamide as anticipated from their Guttmann donor numbers (D_N) of 14.1,[33] 23.5[34,35] and 26.6,[33] respectively. (Similar decreases in stability with increase in D_N are widely observed in the alkali-metal cryptates.[20,22,23]) An unusual aspect is the change in relative stabilities from $[NaL^1]^+ > [LiL^1]^+$ in dimethylformamide and methanol to $[LiL^1]^+ > [NaL^1]^+$ in acetonitrile. There appears to be no report of such a change in relative stabilities with change in solvent for the alkali-metal cryptates for which the relative stability is dominated by the optimization of fit of the metal ion into the cryptand cavity. It seems that the greater flexibility of L^1 results in the nature of the solvent having more influence on the relative stabilities of $[ML^1]^+$ than is the case with the cryptates. Acetonitrile is distinguished from dimethylformamide and methanol by its low D_N of 14.1 (which has the general effect of increasing $[ML^1]^+$ stability as discussed above), its inability to hydrogen bond and its nitrogen donor atom. By virtue of its higher atomic number, Na^+ is a less hard acid than Li^+ and may therefore interact sufficiently more strongly with the borderline hard base[29,30] acetonitrile nitrogen to result in the stability order of $[LiL^1]^+ > [NaL^1]^+$. {It is unlikely that hydrogen bonding is an important factor as the complexes of the methoxy analogue of L^1, 7,13-bis(2-methoxyethyl)-1,4,10-trioxa-7,13-diazacyclopentadecane, L^9, are characterized by the relative stabilities $[LiL^9]^+ > [NaL^9]^+$, which is the reverse of the order observed in dimethylformamide and methanol.[36]} In methanol log(K/dm^3 mol^{-1}) = 2.08 ± 0.03, 4.87 and 5.08[12] for $[LiL^2]^+$, $[NaL^2]^+$ and $[KL^2]^+$, respectively, where the last two values are larger than the analogous values in dimethylformamide, as anticipated from the D_N of the two solvents. In the case of $[LiL^2]^+$, the relative stabilities in methanol and dimethylformamide are the reverse of those anticipated, which indicates that D_N represents a general measure of solvent characteristics on which more specific characteristics may superimpose.

Metal-ion Exchange in the $[ML^1]^+$ *and* $[ML^2]^+$ *Ions.*— Complete lineshape analyses[19] of the temperature-dependent coalescences of the ^{7}Li resonances arising from solvated Li^+ and $[LiL^1]^+$ as Li^+ exchanges between these environments (Fig. 1) in dimethylformamide and methanol yields τ_c, the mean lifetime of Li^+ in $[LiL^1]^+$, for the solutions of compositions given in Table 2. (For each solution $\tau_c/x_c = \tau_s/x_s$, where τ_s is the mean lifetime of Li^+ in the solvated environment, and x_c and x_s are the corresponding mole fractions.) The magnitudes and temperature variations of τ_c for each of the dimethylformamide solutions of $[LiL^1]^+$ studied are very similar, as is also the case for the methanol solutions (Fig. 2). This indicates that the mean lifetime of $[LiL^1]^+$, $\tau_c = 1/k_d$ (where k_d is the decomplexation rate constant), is independent of the concentration of solvated Li^+ (Table 2) consistent with the non-participation of the latter species in the rate-determining step of the dominant pathway for exchange of Li^+ on $[LiL^1]^+$. This is compatible with the operation of a monomolecular mechanism for the decomplexation of Li^+ from $[LiL^1]^+$ [equation (2)] where $k_c(=k_dK)$ is a

$$Li^+ + L^1 \underset{k_d}{\overset{k_c}{\rightleftharpoons}} [LiL^1]^+ \qquad (2)$$

composite complexation rate constant, as is discussed below. Similar conclusions are drawn from the τ_c and k_d data derived from the coalescences of the ^{23}Na resonances characterizing solvated Na^+ and $[NaL^1]^+$ in acetonitrile, and Na^+ and $[NaL^2]^+$ in methanol (Fig. 2 and Table 2). The kinetic parameters for the decomplexation of $[LiL^1]^+$, $[NaL^1]^+$ and $[NaL^2]^+$ (Table 2) are derived from the temperature variation of τ_c through equation (3) where all symbols have their usual meanings.

$$k_d = 1/\tau_c = (k_BT/h)\exp[(-\Delta H_d^{\ddagger}/RT) + (\Delta S_d^{\ddagger}/R)] \qquad (3)$$

Table 2 Solution compositions and kinetic parameters for the exchange of M^+ on $[ML^n]^+$

Solution	$[ML^n]^+$	Solvent	$[M^+_{(solvated)}]$ mol dm^{-3}	$[ML^{n+}]$/ mol dm^{-3}	k_d/s^{-1}	$\Delta H_d^{\ddagger}$/ kJ mol^{-1}	$\Delta S_d^{\ddagger}$/ J K^{-1} mol^{-1}
					(225.0 K)*		
i	$[LiL^1]^+$	Dimethylformamide	0.0155	0.0054	218 ± 3	64.6 ± 1.2	89.4 ± 4.8
ii			0.0094	0.0115	223 ± 5	66.1 ± 1.7	96.1 ± 6.7
iii			0.0078	0.0132	228 ± 5	65.2 ± 1.8	92.4 ± 6.9
(i–iii)					223 ± 3	65.4 ± 0.9	92.9 ± 3.6
					(204.0 K)*		
i	$[LiL^1]^+$	Methanol	0.0138	0.0074	26.9 ± 0.3	26.5 ± 0.5	−84.3 ± 2.5
ii			0.0098	0.0115	26.5 ± 0.4	27.3 ± 0.8	−80.5 ± 3.9
iii			0.0076	0.0136	26.5 ± 0.6	27.6 ± 1.3	−79.1 ± 6.0
(i–iii)					26.7 ± 0.2	27.1 ± 0.5	−81.5 ± 3.6
					(304.0 K)*		
i	$[NaL^1]^+$	Acetonitrile	0.0767	0.0242	325 ± 7	53.7 ± 1.6	−20.2 ± 5.6
ii			0.0383	0.0625	313 ± 5	52.3 ± 1.0	−25.4 ± 3.3
iii			0.0282	0.0726	312 ± 4	51.8 ± 0.8	−27.0 ± 2.9
(i–iii)					317 ± 3	52.6 ± 0.7	−24.1 ± 2.4
					(256.0 K)*		
i	$[NaL^2]^+$	Methanol	0.0779	0.0220	179 ± 10	49.2 ± 3.1	−8.5 ± 12.4
ii			0.0503	0.0545	208 ± 4	43.6 ± 1.3	−28.9 ± 5.2
iii			0.0280	0.0719	208 ± 6	41.6 ± 2.4	−36.6 ± 9.9
(i–iii)					206 ± 3	42.8 ± 1.1	−32.0 ± 4.5

* Coalescence temperature.

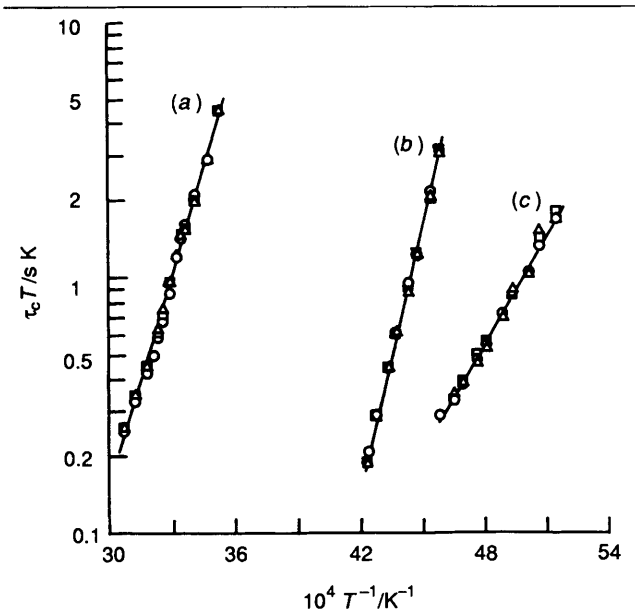
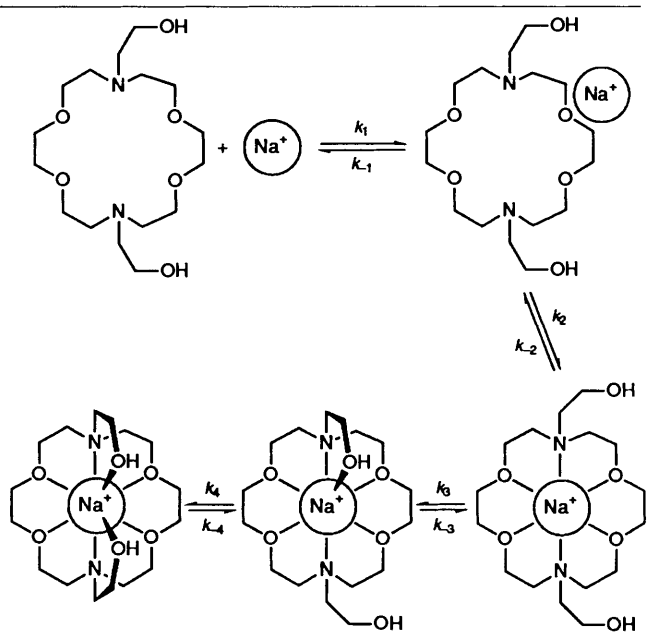


Fig. 2 The temperature variation of τ_c for (*a*) Na^+–$[NaL^1]^+$–acetonitrile solutions, (*b*) Li^+–$[LiL^1]^+$–dimethylformamide solutions, and (*c*) Li^+–$[LiL^1]^+$–methanol solutions ($\tau_c/10$ in this case). Data points for solutions i–iii are represented by circles, squares and triangles, respectively, for each system. The solid lines represent the best fits of the combined data by equation (3) for each group of solutions



Scheme 1

A quantitative study of the exchange of Na^+ on $[NaL^1]^+$ in dimethylformamide and methanol was precluded by these systems being in the fast-exchange limit of the NMR time-scale over the solvent liquid temperature range. Thus only an estimate of $k_d \geqslant 1000\ s^{-1}$ at 298.2 K was possible in each case. In all three solvents, $[LiL^2]^+$ was in the extreme limit of fast exchange and no estimates of k_d were possible, but in acetonitrile and dimethylformamide estimates of $k_d \geqslant 1000\ s^{-1}$ at 298.2 K were possible for $[NaL^2]^+$ although it was also in the fast-exchange limit. (It should be noted that entry into the fast-exchange regime of the NMR time-scale is a result of the chemical lability of the system and the magnitude of the difference in chemical shifts of the observed nucleus in the environments between which exchange occurs. As no quantitations of the chemical shift differences characterizing the systems discussed in this paragraph were possible, the estimated k_d values are limiting values only and are not further discussed.)

The complexation and decomplexation of Li^+ or Na^+ by L^1 or L^2 involves sequential solvation, co-ordination and conformation changes, some of which are indicated in Scheme 1 for the complexation of Na^+ by L^2. This mechanism is based on the *syn* conformation[10,11] of $[NaL^2]^+$, and assumes an initial diffusion-controlled formation (k_1/k_{-1}) of an encounter complex in which a direct interaction between Na^+ and L^2 exists, but Na^+ resides outside the L^2 ring. The sequential entry of Na^+ into the L^2 ring (k_2/k_{-2}) and the co-ordination of the two hydroxy groups (k_3/k_{-3}, k_4/k_{-4}) then follow to produce eight-co-ordinate Na^+ in $[NaL^2]^+$. (This is similar to the Eigen–Winkler mechanism in which the fast initial complexation step is followed by a slower conformational change in the ligand.[37])

Table 3 Kinetic parameters for M^+ exchange on $[ML^n]^+$

$[ML^n]^+$	Solvent	$\log(K/dm^3\ mol^{-1})$ (298.2 K)	$10^{-5}k_c$ (298.2 K)[a]/ $dm^3\ mol^{-1}\ s^{-1}$	k_d (298.2 K)/s^{-1}	$\Delta H_d^{\ddagger}$/ kJ mol^{-1}	$\Delta S_d^{\ddagger}$/ J $K^{-1}\ mol^{-1}$
$[LiL^1]^+$ [b]	Dimethylformamide	2.36 ± 0.03	3 436	1 500 000	65.4	92.9
$[LiL^1]^+$ [b]	Methanol	2.85 ± 0.05	43	6 070	27.1	−81.5
$[LiL^3]^+$ [c]	Methanol	5.38	192	78.4	23.8	−129
$[NaL^1]^+$ [b]	Acetonitrile	7.00 ± 0.01	145 000	207	52.6	−24.1
$[NaL^2]^+$	Methanol	4.87[d]	3 058[b]	4 130[b]	42.8[b]	−32.0[b]
$[NaL^4]^+$ [e]	Methanol	7.9	2 700	2.87		
$[NaL^6]^+$ [f]	Methanol	3.4	271	10 800	46.7	−11

[a] $k_c = k_dK$. [b] This work. [c] Ref. 41. [d] Ref. 12. [e] Ref. 42. [f] Ref. 23.

The choice between this mechanism and alternative sequences in which one or both hydroxyl groups co-ordinate at an earlier stage cannot be eliminated on the basis of the current data.

A sequential complexation process has been detected in an ultrasonic relaxation study of the complexation of Na^+ by 7-methoxyethoxyethyl-1,4,10-trioxa-7-azacyclopentadecane in methanol at 298.2 K, where $k_1 = 9.0 \times 10^{10}$ $dm^3\ mol^{-1}\ s^{-1}$, $k_{-1} = 2.1 \times 10^8\ s^{-1}$, $k_2 = 1.2 \times 10^7\ s^{-1}$ and $k_{-2} = 1.5 \times 10^5\ s^{-1}$, and the first pair of rate constants refer to the formation of an encounter complex and the second pair to the entry of Na^+ into the ring and the complexation of Na^+ by the methoxyethoxyethyl arm.[13] A similar sequence was detected in an ultrasonic relaxation study of the complexation of Na^+ by 1,4,7,10,13,16-hexaoxaoctadecane in methanol at 298.2 K where $k_2 = 2.8 \times 10^8\ s^{-1}$ was assigned to the entry of Na^+ into the ring from the encounter complex, and $k_3 = 1.6 \times 10^6\ s^{-1}$ was assigned to a conformational change in the complex.[38,39] Subsequently a ^{23}Na NMR study yielded a decomplexation rate constant of $7.2 \times 10^4\ s^{-1}$ which was assigned as k_{-3} characterizing the reverse of the conformational change corresponding to k_3.[40] Thus it is probable that the k_d determined for $[NaL^2]^+$ by ^{23}Na NMR spectroscopy in this study characterizes one of the slower steps in the sequence shown, and is probably equivalent to k_{-3} or k_{-4}. Similar assignments are plausible for k_d of $[NaL^1]^+$ and $[LiL^1]^+$ (Table 3). On this basis it is apparent that $k_c(=k_dK)$ is a composite rate constant incorporating the several sequential rate processes of the complexation mechanism.

The data in Table 3 afford a limited comparison of the kinetic characteristics of $[ML^1]^+$ and $[ML^2]^+$ with those of other complexes.[41,42] Thus, it is seen that the differences in stability among $[NaL^2]^+$, $[NaL^4]^+$ and $[NaL^6]^+$ in methanol are dominated by the variation in k_d, with the much smaller k_d characterizing $[NaL^4]^+$ being attributable to a combination of the rigid nature of L^4 and its eight donor atoms. The relative magnitudes of k_d and K for $[LiL^1]^+$ and $[LiL^3]^+$ in methanol may be similarly explained.

Although K of $[LiL^1]^+$ in dimethylformamide is only one third of that in methanol, both the k_c and k_d values observed in dimethylformamide are much greater than those observed in methanol. In contrast k_c characterizing an alkali-metal cryptate shows a small variation with solvent by comparison with that of k_d, such that K is substantially determined by the latter variation.[42,43] These limited $[LiL^1]^+$ data suggest that substantial variation of both k_c and k_d may occur with change of solvent, reflecting the greater flexibility of the lariat ethers.

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