Monovalent Metal-ion Complexation by a Bibracchial Lariat Ether in Several Solvents

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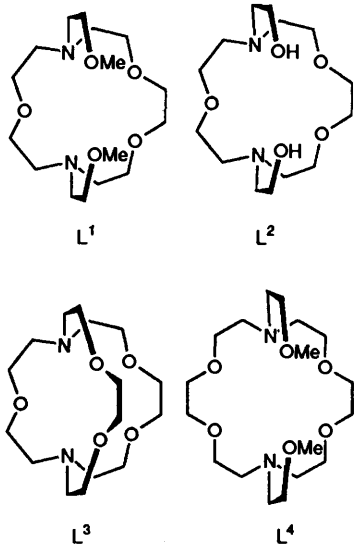
The stabilities of monovalent metal complex ions, $[ML^1]^+$, of 7,13-bis(2-methoxyethyl)-1,4,10-trioxa-7,13-diazacyclopentadecane (L^1) have been determined by potentiometric titration. The stability varies with the identity of M^+ in the sequence Li^+ (9.13, 7.0, 3.01, 2.23), Na^+ (8.17, 7.1, 4.89, 3.50), K^+ (5.24, 5.0, 4.69, 3.31), Rb^+ (4.39, 4.2, 3.97, 2.84), Cs^+ (3.77, 3.6, 3.46, 2.31) and Ag^+ (7.08, 12.2, 9.86, 8.37), where the figures in parentheses are $\log(K/dm^3\ mol^{-1})$ and K is the stability constant for $[ML^1]^+$ in acetonitrile, propylene carbonate, methanol and dimethylformamide, respectively, at 298.2 K and $I = 0.05$ mol dm^{-3} (NEt_4ClO_4). The decomplexation of Li^+ in $[LiL^1]^+$, determined by ^7Li NMR spectroscopy, is characterized by k_d (298.2 K) = 79.7, 1970 and 32 600 s^{-1}, $\Delta H_d^{\ddagger} = 35.8$, 20.4 and 36.4 kJ mol^{-1}, and $\Delta S_d^{\ddagger} = -88.6$, −113 and −36.5 J K^{-1} mol^{-1}, respectively, in propylene carbonate, methanol and dimethylformamide. Sodium-23 NMR spectroscopy yields k_d (298.2 K) = 124, 60.0 and 61.8 s^{-1}, $\Delta H_d^{\ddagger} = 43.2$, 53.4 and 55.8 kJ mol^{-1}, and $\Delta S_d^{\ddagger} = -60.0$, −32.0 and −23.5 J K^{-1} mol^{-1} for the decomplexation of $[NaL^1]^+$ in acetonitrile, propylene carbonate and pyridine, respectively. These variations in complex-ion stability and lability are discussed in terms of ligand, metal-ion and solvent characteristics.

Bibracchial lariat ethers[1-7] are either crown ethers or diazacrown ethers with a sidearm attached to each of two ring carbons or ring nitrogens, respectively. They occupy a niche between the crown ethers[1,8] and cryptands[9-16] in their ability to complex alkali-metal ions. The complexes formed by all three types of ligands exhibit variations in stability which may be correlated with the size of the alkali-metal ion. For the cryptates this variation is largely dependent on the matching of the size of the alkali-metal ion to that of the cryptand cavity so that an optimized match produces the cryptate of highest stability and establishes a selectivity pattern which shows little variation with solvent, despite a change in solvent producing changes in individual cryptate stability.[12-15] In contrast, a recent study of bibracchial lariat ether complexes showed that the alkali-metal-ion selectivity pattern was solvent dependent.[7] Accordingly, we have sought further insight into the factors determining selectivity in bibracchial lariat ether systems through an equilibrium and kinetic study of the alkali-metal ion complexation by the bibracchial lariat ether 7,13-bis(2-methoxyethyl)-1,4,10-trioxa-7,13-diazacyclopentadecane[5] (L^1) in a range of solvents. Comparisons are made with the complexing characteristics of the closely related bibracchial lariat ether 7,13-bis(2-hydroxyethyl)-1,4,10-trioxa-7,13-diazacyclopentadecane (L^2),[2-5] and the cryptand 4,7,13,16,21-pentaoxa-1,10-diazabicyclo[8.8.5]tricosane (L^3).[9-11,16]



L^1 L^2 L^3 L^4

Experimental

Preparation of Materials.—The compound L^1 was prepared by a literature method,[2] and the sources of the metal salts were as described previously.[7] The salt NEt_4ClO_4 was prepared by treating aqueous NEt_4Br (BDH) with an excess of $HClO_4$, and the resultant NEt_4ClO_4 precipitate was recrystallized from water until no acid or bromide was detectable. All of the metal perchlorates and NEt_4ClO_4 were vacuum dried at 353–363 K for 48 h, and were stored over P_2O_5 under vacuum. **CAUTION**: Anhydrous perchlorate salts are potentially powerful oxidants and should be handled with care.

Acetonitrile, propylene carbonate, methanol, dimethylformamide and pyridine (BDH) were purified and dried as in the literature,[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 the other solvents. The water content of these solvents was below the Karl–Fischer detection level of approximately 50 ppm. Solutions for potentiometric titration and NMR spectroscopic study were prepared as described.[7]

Potentiometric Titrations.—Stability constants defined as in equation (1) for M = Ag were determined by duplicated

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

potentiometric titrations of $AgNO_3$ solution with L^1 solution, and for M = Li, Na, K, Rb and Cs were determined in competitive titrations against Ag^+ using methods and conditions similar to those in the literature.[7,18] This competitive

Table 1 The variation of the stabilities of $[ML^1]^+$, $[ML^2]^+$ and $[ML^3]^+$ in several solvents at 298.2 K

			log(K/dm^3 mol^{-1})[a]					
Complex	Solvent	D_N	M = Li	Na	K	Rb	Cs	Ag
$[ML^1]^+$[b]	Acetonitrile	14.1[c]	9.13 ± 0.05	8.17 ± 0.05	5.24 ± 0.05	4.39 ± 0.05	3.77 ± 0.05	7.08 ± 0.05
$[ML^1]^+$[b]	Propylene carbonate	15.1[c]	7.0 ± 0.1	7.1 ± 0.1	5.0 ± 0.1	4.2 ± 0.01	3.6 ± 0.01	12.2 ± 0.1
$[ML^1]^+$[b]	Methanol	23.5[d]	3.01 ± 0.05	4.89 ± 0.05	4.69 ± 0.05	3.97 ± 0.05	3.46 ± 0.05	9.86 ± 0.05
$[ML^1]^+$[b]	Dimethylformamide	26.6[c]	2.23 ± 0.05	3.50 ± 0.05	3.31 ± 0.05	2.84 ± 0.05	2.31 ± 0.05	8.37 ± 0.05
$[ML^1]^+$[b,e]	Water	33.0[d]	< 2	< 2	< 2	< 2	< 2	7.57 ± 0.05
$[ML^1]^+$[b]	Pyridine	33.1[c]	5.08 ± 0.05	6.71 ± 0.05				1.8 ± 0.1
$[ML^2]^+$[f]	Acetonitrile	14.1[c]	8.61	7.00				6.24
$[ML^2]^+$[f]	Methanol	23.5[d]	2.85	4.71				9.36
$[ML^2]^+$[f]	Dimethylformamide	26.6[c]	2.36	3.93	3.08	2.50	2.11	9.34
$[ML^3]^+$[g]	Acetonitrile	14.1[c]	10.33	> 11.3	9.5	7.27	5.15	11.24
$[ML^3]^+$[g]	Propylene carbonate	15.1[c]	9.60	12.09	9.88	7.03	4.92	18.50
$[ML^3]^+$[h]	Methanol	23.5[d]	5.38	9.65	8.54	6.74	4.33	14.64
$[ML^3]^+$[g]	Dimethylformamide	26.6[c]	3.58	7.93	6.66	5.35	3.61	12.41

[a] Errors represent one standard deviation. [b] This work. [c] Ref. 21. [d] Ref. 22. [e] For $H_2L^{1\,2+}$ $pK_{a1} = 8.42 \pm 0.05$ and $pK_{a2} = 7.16 \pm 0.05$. [f] Ref. 7. [g] Ref. 13. [h] Ref. 18.

method of determining K requires $[AgL^1]^+$ to be significantly more stable than its alkali-metal analogue. This was not the case for $[LiL^1]^+$ and $[NaL^1]^+$ in acetonitrile and pyridine, and accordingly their stability constants were determined using a Na^+-specific electrode as described.[7] Stabilities in water were determined by a glass-electrode potentiometric method.[19] All titrations were carried out at 298.2 K and $I = 0.05$ mol dm^{-3} except those in water for which $I = 0.10$ mol dm^{-3} (NEt_4ClO_4).

NMR Spectroscopy.—Variable-temperature ^{7}Li and ^{23}Na NMR spectra were run at 116.59 and 79.39 MHz, respectively, on a Bruker CXP-300 spectrometer and were subjected to lineshape analysis as previously described.[7,20]

Results and Discussion

$[ML^1]^+$ *Stability.*—The data in Table 1 show two effects of solvent variation on the stability constants for $[ML^1]^+$. The first is that K for a given alkali metal decreases as the Gutmann donor number (D_N)[21,22] increases, except for pyridine. For the first five solvents this is consistent with an increase in the ability of the solvent to compete with L^1 for M^+ as its electron-donating power increases. Pyridine is a borderline soft base[23,24] as a result of the incorporation of the nitrogen-donor atom into the aromatic ring, which may also introduce a greater degree of steric crowding into pyridine solvation than that experienced by other solvents. Thus, pyridine competes strongly for the soft acid Ag^+, but less effectively for the hard acids Li^+ and Na^+. As a consequence, the stabilities of $[LiL^1]^+$ and $[NaL^1]^+$ are higher, and that of $[AgL^1]^+$ is lower, than anticipated from $D_N = 33.1$ for pyridine which is based on the formation of a 1 : 1 complex with $SbCl_5$ in dichloroethane.[21] The tendency for Ag^+ to bind soft-base nitrogen-donor ligands more strongly than oxygen donors[25,26] is also the reason that $[AgL^1]^+$ is less stable in acetonitrile than anticipated on the basis of $D_N = 14.1$. Consistent with these trends, the stability of $[AgL^1]^+$ decreases with increase in D_N in the four hard-base oxygen-donor solvents, and is higher than those of its alkali-metal analogues for which these solvents compete more effectively.

The second effect of the solvent is that in the first four solvents the relative stabilities of $[ML^1]^+$ change systematically as solvent D_N increases. Thus, in acetonitrile the relative stability of $[ML^1]^+$ varies with M^+ in the sequence $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$, in propylene carbonate the sequence is $Li^+ \approx Na^+ > K^+ > Rb^+ > Cs^+$, and in methanol and dimethylformamide the sequence is $Li^+ < Na^+ > K^+ > Rb^+ > Cs^+$, consistent with the stronger-donor solvents competing more effectively for Li^+ relative to Na^+ and K^+. The data obtained in pyridine also follow this pattern, as do those for $[ML^2]^+$.[7] The stabilities of $[ML^1]^+$ and $[ML^2]^+$ are usually within a factor of 10 of each other, which demonstrates the differing influences of the methoxyethyl and hydroxyethyl pendant arms of L^1 and L^2 on complex stability and some change in their importance relative to the influence of the solvent.

The variations in the selectivity patterns exhibited by L^1 arise from the changing balance between the solvating power of the solvent, the solvation energy of M^+, the binding energy of L^1 and the formation of a cavity of an appropriate size to accommodate M^+. It is anticipated that the strain in $[ML^1]^+$ varies with the size of the cavity formed, but as the species $[ML^1]^+$ (M = Li, Na or K) exhibit the higher stabilities, depending on the solvent, it appears that there is a considerable variation in the cavity size before such strain significantly destabilizes $[ML^1]^+$. In contrast, the relative stabilities of the cryptate $[ML^3]^+$ vary with M^+ in the sequence $Li^+ < Na^+ > K^+ > Rb^+ > Cs^+$ in acetonitrile, propylene carbonate, methanol and dimethylformamide (Table 1) consistent with the relatively rigid preformed cavity of L^3 being optimized to accommodate Na^+, and thereby determining the L^3 selectivity pattern to a major extent. Generally, the stability of $[ML^3]^+$ is substantially greater than that of $[ML^1]^+$ consistent with the stereochemistry of L^3 being more favourable to the binding of alkali-metal ions than is that of the more flexible L^1 (the cryptate effect).[11-13]

X-ray crystallographic studies[16] show that Na^+ occupies the centre of the L^3 cavity in $[NaL^3]^+$, whereas K^+ resides outside the cavity adjacent to the eighteen-membered ring of L^3 in $[KL^3]^+$. The cavity of L^3 is estimated to have a radius[9-11] of *ca.* 1.1 Å which 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 close to an optimum fit in the L^3 cavity while Li^+ is too small and K^+, Rb^+ and Cs^+ are too large. (The seven-co-ordinate radii should be used for comparison, but they are only available where quoted in parentheses.) This coincides with $[NaL^3]^+$ being the most stable of the alkali-metal L^3 cryptates in solution.

No solid-state structures for $[ML^1]^+$ and $[ML^2]^+$ appear to have been reported. In the larger and closely related 7,16-bis(2-methoxyethyl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (L^4) complexes, $[NaL^4]^+$ and $[KL^4]^+$, the metal ions are bound by two nitrogens and six oxygens.[3,4] Both methoxy groups are above the plane of the ring (the *syn* conformation) in the first case and on opposite sides of the ring plane in the

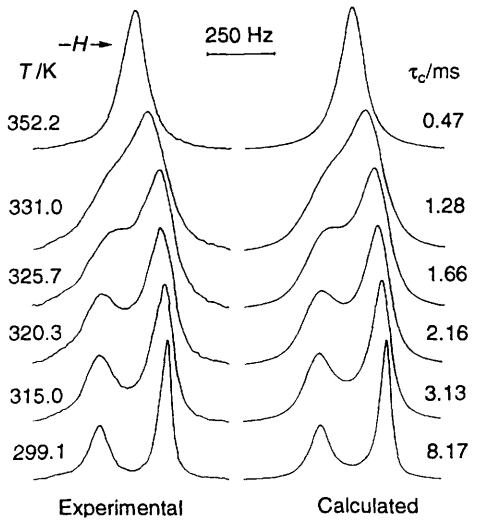


Fig. 1 Typical exchange-modified 79.39 MHz ^{23}Na NMR spectra of an acetonitrile solution of solvated Na^+ (0.0586 mol dm^{-3}) and $[NaL^1]^+$ (0.0442 mol dm^{-3}). Experimental temperatures and spectra appear to the left, and the best-fit calculated lineshapes and corresponding τ_c values to the right. The resonance of $[NaL^1]^+$ appears upfield from that of solvated Na^+

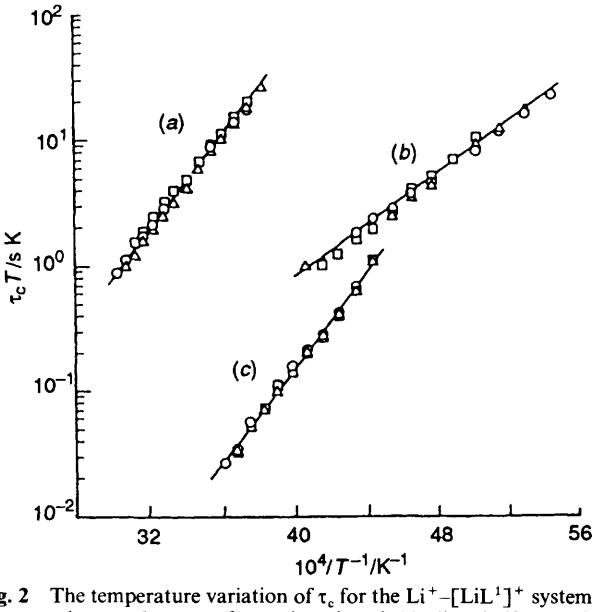


Fig. 2 The temperature variation of τ_c for the Li^+–$[LiL^1]^+$ system in (*a*) propylene carbonate, (*b*) methanol and (*c*) dimethylformamide. Data points for solutions i–iii, the compositions of which are given in Table 2, are represented by triangles, circles and squares, respectively, for each system. The solid lines represent the best fits of the combined data by equation (3) for each group of solutions

second case (the *anti* conformation). The analogous complexes of 7,16-bis(2-hydroxyethyl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane with Na^+ and K^+ adopt the *syn* conformation.[3,4]

Metal-ion Exchange on $[LiL^1]^+$ *and* $[NaL^1]^+$.—Complete NMR lineshape analyses[20] of the temperature-dependent coalescences of the ^{7}Li NMR resonances of solvated Li^+ and $[LiL^1]^+$ and of the ^{23}Na NMR resonances of solvated Na^+ and $[NaL^1]^+$ as the metal ions exchange between these environments (Fig. 1) in several solvents yield the mean lifetimes of $[LiL^1]^+$ and $[NaL^1]^+$, τ_c, for the solutions of composition given in Tables 2 and 3 ($\tau_c/X_c = \tau_s/X_s$, where τ_s is the mean lifetime of the solvated metal ion, and X_c and X_s are

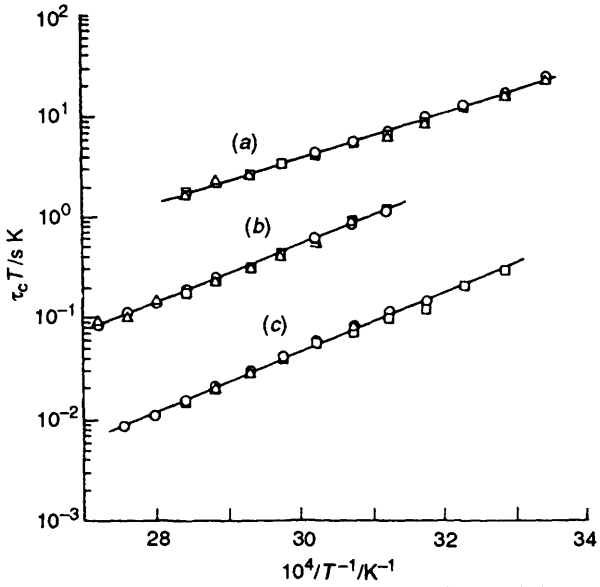


Fig. 3 The temperature variation of τ_c for the Na^+–$[NaL^1]^+$ system in (*a*) acetonitrile (×10), (*b*) propylene carbonate and (*c*) pyridine (÷10). Data points for solutions i–iii, the compositions of which are given in Table 3, are represented by triangles, circles and squares, respectively, for each system. The solid lines represent the best fits of the combined data by equation (3) for each group of solutions

the corresponding mole fractions). The magnitudes and temperature variations of τ_c for each set of $[LiL^1]^+$ and $[NaL^1]^+$ solutions studied are very similar (Figs. 2 and 3). This shows that τ_c for $[LiL^1]^+$ and $[NaL^1]^+$ is largely independent of the concentration of solvated Li^+ and Na^+. Thus, the dominant exchange process occurs through a monomolecular decomplexation mechanism, as shown in equation (2) where $M^+ = Li^+$

$$M^+ + L^1 \underset{k_d}{\overset{k_c}{\rightleftharpoons}} [ML^1]^+ \quad (2)$$

or Na^+. The decomplexation rate constant $k_d = 1/\tau_c = k_c/K$ where k_c is a composite complexation rate constant, as is discussed below. The decomplexation activation parameters (Tables 2 and 3) are derived from the temperature variation of τ_c through equation (3) where all symbols have their usual

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

meanings. Quantitative studies of exchange were precluded by $[LiL^1]^+$ being in the slow-exchange limit in pyridine, and by $[NaL^1]^+$ being in the fast-exchange limit in methanol and dimethylformamide.

The first step in the complexation of M^+ by L^1 is the formation of an encounter complex in which M^+ retains its first solvation shell while in contact with L^1.[7] Sequential desolvation, binding of M^+ and conformational changes in L^1 occur in slower steps leading to the formation of $[ML^1]^+$, and decomplexation of $[ML^1]^+$ occurs in the reverse sequence in which the slowest step is characterized by k_d. With the exception of the formation of the encounter complex, the complexation and decomplexation steps are first order processes and as a consequence k_c ($=k_dK$) is a composite rate constant incorporating the slowest complexation step and the equilibrium constant for the formation of the encounter complex. While only the slowest complexation and decomplexation steps are characterized in this study, the sequential nature of this type of process has been confirmed in similar systems by the detection of several steps in ultrasonic relaxation studies of the complexation of Na^+ by 1,4,7,10,13,16-hexaoxacyclooctadecane and 13-[2-(2-methoxyethoxy)ethyl]-1,4,7,10-tetraoxa-13-azacyclopenta-decane in methanol.[6,28,29]

Table 2 Lithium-ion exchange on $[LiL^1]^+$ in propylene carbonate, methanol and dimethylformamide. Solution compositions and kinetic parameters[a]

Solution	Solvent	$[Li^+_{solvated}]$/ mol dm^{-3}	$[LiL^{1+}]$/ mol dm^{-3}	k_d/ s^{-1}	$\Delta H_d^‡$/ kJ mol^{-1}	$\Delta S_d^‡$/ J K^{-1} mol^{-1}
				(288.2 K)[b]		
i	Propylene carbonate	0.013 70	0.007 70	50.8 ± 0.5	36.4 ± 0.3	−85.6 ± 0.8
ii		0.009 20	0.012 20	45.8 ± 1.1	35.7 ± 0.7	−88.2 ± 1.5
iii		0.006 85	0.014 55	42.9 ± 0.5	34.6 ± 0.4	−92.2 ± 0.7
(i–iii)[c]		—	—	46.7 ± 0.8	35.8 ± 0.6	−88.6 ± 1.2
				(215.1 K)[b]		
i	Methanol	0.013 33	0.007 18	58.6 ± 2.1	20.7 ± 0.7	−112 ± 3
ii		0.009 84	0.010 66	57.3 ± 0.7	18.3 ± 0.3	−122 ± 2
iii		0.005 13	0.015 38	57.0 ± 1.2	22.5 ± 0.5	−106 ± 3
(i–iii)[c]		—	—	59.1 ± 1.1	20.4 ± 0.4	−113 ± 2
				(230.8 K)[b]		
i	Dimethylformamide	0.014 41	0.007 10	354 ± 10	35.9 ± 0.6	−38.5 ± 2.2
ii		0.011 40	0.010 11	331 ± 12	36.8 ± 0.8	−35.3 ± 3.2
iii		0.007 74	0.013 76	349 ± 15	36.9 ± 1.1	−34.3 ± 4.6
(i–iii)[c]		—	—	346 ± 9	36.4 ± 0.5	−36.5 ± 2.0

[a] Errors represent one standard deviation from the least-squares fit of the experimental τ_c data by equation (3). [b] k_d is quoted for a temperature in the midst of the spectral coalescence region where the most accurate data are obtained. [c] Kinetic parameters derived from the simultaneous least-squares fit of the data for solutions i–iii by equation (3).

Table 3 Sodium-ion exchange on $[NaL^1]^+$ in acetonitrile, propylene carbonate and pyridine. Solution compositions and kinetic parameters (see footnotes *a–c* to Table 2)

Solution	Solvent	$[Na^+_{solvated}]$/ mol dm^{-3}	$[NaL^{1+}]$/ mol dm^{-3}	k_d/ s^{-1}	$\Delta H_d^‡$/ kJ mol^{-1}	$\Delta S_d^‡$/ J K^{-1} mol^{-1}
				(331.0 K)		
i	Acetonitrile	0.0730	0.0298	783 ± 11	41.0 ± 0.8	−66.4 ± 2.5
ii		0.0586	0.0442	768 ± 11	44.9 ± 0.6	−55.0 ± 2.1
iii		0.0134	0.0894	778 ± 11	43.7 ± 0.7	−58.6 ± 2.3
(i–iii)		—	—	775 ± 10	43.2 ± 0.6	−60.0 ± 2.1
				(336.3 K)		
i	Propylene carbonate	0.0622	0.0397	771 ± 13	56.0 ± 1.7	−26.1 ± 4.8
ii		0.0448	0.0571	768 ± 5	53.2 ± 0.4	−32.5 ± 1.1
iii		0.0153	0.0866	787 ± 8	51.6 ± 0.9	−34.9 ± 2.8
(i–iii)		—	—	777 ± 11	53.4 ± 0.8	−32.0 ± 2.5
				(325.7 K)		
i	Pyridine	0.0816	0.0262	437 ± 4	59.1 ± 0.6	−18.3 ± 1.7
ii		0.0586	0.0460	439 ± 11	56.7 ± 1.5	−21.0 ± 4.8
iii		0.0241	0.0805	469 ± 8	54.2 ± 1.0	−27.1 ± 3.1
(i–iii)		—	—	450 ± 8	55.8 ± 0.9	−23.5 ± 2.8

Table 4 Kinetic parameters for M^+ exchange on $[ML^n]^+$

$[ML^n]^+$	Solvent	D_N	$10^{-5}k_c$(298.2 K)[a]/ dm^3 mol^{-1} s^{-1}	k_d(298.2 K)/ s^{-1}	$\Delta H_d^‡$/ kJ mol^{-1}	$\Delta S_d^‡$/ J K^{-1} mol^{-1}
$[LiL^1]^+$[b]	Propylene carbonate	15.1[c]	7 970	79.7	35.8	−88.6
$[LiL^1]^+$[b]	Methanol	23.5[d]	20.2	1 970	20.4	−113
$[LiL^1]^+$[b]	Dimethylformamide	26.6[c]	55.5	32 600	36.4	−36.5
$[LiL^2]^+$[e]	Methanol	23.5[c]	43	6 070	27.1	−81.5
$[LiL^2]^+$[e]	Dimethylformamide	26.6[c]	3 436	1 500 000	65.4	92.9
$[LiL^3]^+$[f]	Methanol	23.5[d]	192	78.4	23.8	−129
$[NaL^1]^+$[b]	Acetonitrile	14.1[c]	183 400	124	43.2	−60.0
$[NaL^1]^+$[b]	Propylene carbonate	15.1[c]	7 554	60.0	53.4	−32.0
$[NaL^1]^+$[b]	Pyridine	33.1[c]	3 170	61.8	55.8	−23.5
$[NaL^2]^+$[e]	Acetonitrile	14.1[c]	20 700	207	52.6	−24.1
$[NaL^3]^+$[g]	Propylene carbonate	15.1[c]	> 123 000	< 0.01		

[a] $k_c = k_d K$. [b] This work. [c] Ref. 21. [d] Ref. 22. [e] Ref. 7. [f] Ref. 30. [g] Ref. 12.

The k_c and k_d for $[LiL^1]^+$ are smaller than those for $[LiL^2]^+$ in methanol and dimethylformamide. This difference coincides with the replacement of the two methoxy groups of L^1 by hydroxy groups in L^2, and is compatible with the involvement of a pendant arm in the rate-determining steps for the complexation and decomplexation processes. It is unlikely that the slowest complexation step involves a pendant arm making the first bond between Li^+ and L^1 or L^2 (or the slowest decomplexation step breaking it). However, after complexation of Li^+ by the crown ether ring the flexibility of L^1 and L^2 is decreased and subsequent complexation by a pendant arm is probably slowed by conformational changes about the ring nitrogen atom. The $\Delta H_d^‡$ and $\Delta S_d^‡$ for $[LiL^1]^+$ are smaller and more negative, respectively, by comparison with those for $[LiL^2]^+$, differences which are attributable to the influence of the greater inductive effect of the methyl group of the

methoxyethyl pendant arm on the interaction with Li^+. The differing labilities of $[NaL^1]^+$ and $[NaL^2]^+$ in acetonitrile may be similarly taken as indications of pendant arm involvement in the slowest reaction steps.

A four hundred-fold increase in k_d for $[LiL^1]^+$ occurs as the solvent is changed from propylene carbonate to methanol to dimethylformamide (Table 4), and shows that the stronger electron-pair donor solvent competes more effectively for Li^+ in the transition state. The four hundred-fold decrease in k_c which occurs as the solvent is changed from propylene carbonate to dimethylformamide to methanol is consistent with the two stronger electron-pair donor solvents being less readily displaced by L^1 in the transition state than is propylene carbonate. While any effect of solvent on the stability of the encounter complex also contributes to this variation in k_c, the greater stability of $[LiL^1]^+$ in propylene carbonate, nevertheless, arises from k_c and k_d magnitudes which are larger and smaller, respectively, by comparison with those observed in methanol and dimethylformamide. The variation in $\Delta H_d^{\ddagger}$ and $\Delta S_d^{\ddagger}$ for the decomplexation of $[LiL^1]^+$ with change of solvent shows no obvious correlation with the nature of the solvent.

The similar stabilities of $[LiL^1]^+$ and $[NaL^1]^+$ in propylene carbonate arise from their similar k_c and k_d magnitudes (Table 4), but the decomplexation activation parameters of the two systems differ with the higher $\Delta H_d^{\ddagger}$ of $[NaL^1]^+$ being counterbalanced by a less negative $\Delta S_d^{\ddagger}$. The higher stability of $[NaL^1]^+$ in acetonitrile results from a larger k_c by comparison with k_c characterizing $[NaL^1]^+$ in propylene carbonate and pyridine, and the greater stability of $[NaL^1]^+$ by comparison with that of $[NaL^2]^+$ in acetonitrile arises from its greater k_c and smaller k_d. These variations in the labilities of the sodium species may be explained in similar terms to those employed for their lithium analogues, with any differences being attributable to the greater ionic radius of Na^+.

A larger k_c and substantially smaller k_d cause the cryptate $[LiL^3]^+$ to be more stable than $[LiL^1]^+$ and $[LiL^2]^+$ in methanol.[30] Although Li^+ is too small for an optimum fit into the L^3 cavity, it appears that the L^3 donor atoms are held in an array which favours complexation of Li^+, but retards the decomplexation of $[LiL^3]^+$, by comparison with the more flexible bibracchial lariat ethers. A similar relationship exists between $[NaL^1]^+$ and $[NaL^3]^+$ in propylene carbonate, although Na^+ is now close to an optimum fit for the L^3 cavity (Table 4).

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