Note

Solution studies of monovalent metal complex ions of the bibracchial lariat ether 7,16-bis(2-methoxyethyl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane

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Abstract

The stability of the metal complex ions ($[ML^1]^+$) of 7,16-bis(2-methoxyethyl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (L^1) varies with the nature of M^+ in the sequence Li^+ (5.80, 5.1, 2.47, 1.93, <2), Na^+ (7.91, 6.8, 4.57, 3.31, <2), K^+ (6.19, 6.0, 5.30, 3.82, 2.2), Rb^+ (5.24, 4.7, 4.44, 3.08, <2), Cs^+ (4.41, 4.0, 3.66, 2.38, <2) and Ag^+ (6.90, 11.7, 9.39, 8.28, 7.10), where the first four figures in brackets are log K (dm^3 mol^{-1}) and K is the stability constant for $[ML^1]^+$ at 298.2 K in acetonitrile, propylene carbonate, methanol, dimethylformamide and water, respectivcly. For the decomplexation of $[ML^1]^+$, k_d (298.2 K) = 2650, 2430, 25900 and 347 s^{-1}, in acetonitrile, methanol, dimethylformamide and pyridine, respectively. The factors affecting these variations in stability and lability are discussed.

Key words: Stability constants; Alkali metal complexes; Silver complexes; Macrocyclic ligand complexes

Introduction

The bibracchial lariat ethers exhibit variations in their selectivity for complexing alkali metal ions as the solvent changes [1, 2]. To further elucidate the factors controlling this selectivity we have studied the variation of the stability and lability of the alkali metal complexes of the eighteen-membered ring system 7,16-bis(2-methoxyethyl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (L^1) [3] with solvent to assess the effect of macrocyclic ring size through a comparison with the fifteen-membered 7,13-bis(2-methoxyethyl)-1,4,10-trioxa-7,13-diazacyclopentadecane system (L^2) and also with the 2-hydroxyethyl bibracchial lariat ether systems (L^3 and L^4) [1, 2] in Fig. 1.

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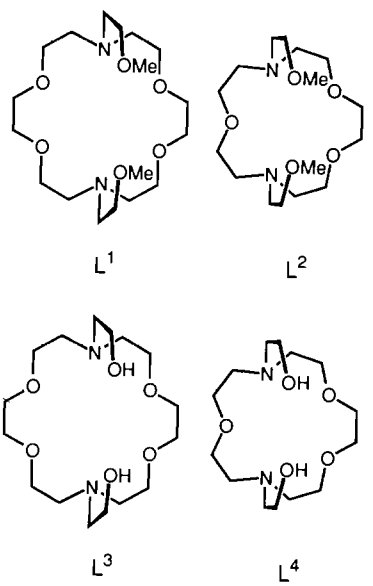

Fig. 1. Structures of the bibracchial lariat ethers L^1–L^4.

Experimental

A literature method was used to prepare L^1 [4]. The sources and preparations of the metal salts and NEt_4ClO_4 were as given previously [1, 2]. Non-aqueous solvents were purified, dried and stored using literature methods [1, 5]. Their water content was below the Karl-Fischer detection level of approximately 50 ppm. Water with a specific resistance of >15 MΩ cm was prepared using a MilliQ-Reagent system. Potentiometric stability constant and NMR kinetic studies were carried out by methods similar to those previously described [1, 2, 6].

Results and discussion

Complex stabilities

The magnitude of K for a given alkali metal $[ML^1]^+$ decreases with increase in the solvent D_N [7, 8], except in the case of pyridine. For acetonitrile, propylene carbonate, methanol and dimethylformamide this indicates 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 [9, 10] as a consequence of the incorporation of the nitrogen atom into the aromatic ring. This may also induce some steric hindrance when pyridine solvates M^+ by comparison with that experienced by the other solvents

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TABLE 1. The variation of the stabilities of $[ML^1]^+$, $[ML^2]^+$, $[ML^3]^+$ and $[ML^4]^+$ in several solvents at 298.2 K

Complex	Solvent	D_N	log K (dm^3 mol^{-1})[a] for M^+					
			Li^+	Na^+	K^+	Rb^+	Cs^+	Ag^+
$[ML^1]^+$ [b]	acetonitrile	14.1[c]	5.80±0.05	7.91±0.05	6.19±0.05	5.24±0.05	4.41±0.05	6.90±0.05
$[ML^1]^+$ [b]	propylene carbonate	15.1[c]	5.1±0.1	6.8±0.1	6.0±0.1	4.7±0.1	4.0±0.1	11.7±0.1
$[ML^1]^+$ [b]	methanol	23.5[d]	2.47±0.05	4.57±0.05	5.30±0.05	4.44±0.05	3.66±0.05	9.39±0.05
$[ML^1]^+$ [b]	dimethylformamide	26.6[c]	1.93±0.05	3.31±0.05	3.82±0.05	3.08±0.05	2.38±0.05	8.28±0.05
$[ML^1]^+$ [b]	water	33.0[d]	<2	<2	2.2±0.1	<2	<2	7.10±0.05
$[ML^1]^+$ [b]	pyridine	33.1[c]	2.79±0.05	6.55±0.05				1.7±0.1
$[ML^2]^+$ [e]	acetonitrile	14.1[c]	9.13	8.17	5.24	4.39	3.77	7.08
$[ML^2]^+$ [e]	propylene carbonate	15.1[c]	7.0	7.1	5.0	4.2	3.6	12.2
$[ML^2]^+$ [e]	methanol	23.5[d]	3.01	4.89	4.69	3.97	3.46	9.86
$[ML^2]^+$ [e]	dimethylformamide	26.6[c]	2.23	3.50	3.31	2.84	2.31	8.37
$[ML^2]^+$ [e]	water	33.0[d]	<2	<2	<2	<2	<2	7.57
$[ML^2]^+$ [e]	pyridine	33.1[c]	5.08	6.71				1.8
$[ML^3]^+$ [f]	dimethylformamide	26.6[c]	2.29	3.65	4.66	3.56	3.36	9.13
$[ML^4]^+$ [f]	dimethylformamide	26.6[c]	2.36	3.93	3.08	2.50	2.11	9.34

[a]Errors represent one standard deviation. [b]This work. [c]Ref. 7. [d]Ref. 8. [e]Ref. 2. [f]Ref. 1.

given in Table 1. The low stability of $[AgL^1]^+$ in pyridine is attributable to the tendency of soft acid Ag^+ to form a strong complex with nitrogen donor ligands [11, 12]. This tendency for Ag^+ to bind nitrogen donors more strongly than oxygen donors is probably the reason that $[AgL^1]^+$ is less stable in acetonitrile than anticipated on the basis of $D_N = 14.1$. The stability of $[AgL^1]^+$ decreases with increase in D_N, and is higher than those of its alkali metal analogues in the hard base oxygen donor solvents because these solvents compete more strongly for the hard acid alkali metal ions.

In acetonitrile and propylene carbonate the relative stability of $[ML^1]^+$ varies with M^+ in the sequence $Li^+ < Na^+ > K^+ > Rb^+ > Cs^+$, while in methanol and dimethylformamide the sequence is $Li^+ < Na^+ < K^+ > Rb^+ > Cs^+$. This contrasts with the sequences observed for $[ML^2]^+$ which are: $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$ in acetonitrile, $Li^+ \approx Na^+ > K^+ > Rb^+ > Cs^+$ in propylene carbonate, and $Li^+ < Na^+ > K^+ > Rb^+ > Cs^+$ in methanol and dimethylformamide. These variations arise from the changing balance between the solvating power of the solvent, the solvation energy of M^+, the binding energy of the ligands, and the optimization of the size of the cavity formed to accommodate M^+ and to minimize strain in $[ML^1]^+$. Depending on the solvent, the highest stability is observed for $[ML^1]^+$ when M^+ is either Na^+ or K^+ (Table 1). This is consistent with a cavity radius within the range of the eight-coordinate radii [13] of Na^+ and K^+ of 1.18 and 1.51 Å, respectively, being most readily adopted by L^1. For the smaller L^2, either $[LiL^2]^+$ or $[NaL^2]^+$ are the most stable complexes formed consistent with a cavity radius within the range of the seven-coordinate radii of Li^+ and Na^+ of 0.84 (which is the average of the six- and eight-coordinate radii in the absence of a literature value for the seven-coordinate radius) and 1.12 Å, respectively, being most readily adopted by L^2.

X-ray crystallographic studies of $[NaL^1]^+$ and $[KL^1]^+$ show that the metal ions are bound by two nitrogens and six oxygens with both methoxy groups above the plane of the ring (the *syn* conformation) in the first case and on opposite sides of the ring plane in the second case (the *anti* conformation) [14–16]. The analogous Na^+ and K^+ complexes of 7,16-bis(2-hydroxyethyl)-1,4,10,13-tetra-7,16-diazacyclooctadecane (L^3) adopt the *syn* conformation, but there appear to be no reported solid state structures for $[ML^2]^+$ and $[ML^4]^+$.

Sodium ion exchange on $[NaL^1]^+$

Complete lineshape analysis [17] of the coalescence of the ^{23}Na resonances of Na^+ in the solvated and $[NaL^1]^+$ environments yields the lifetime of $[NaL^1]^+$, τ_c ($= \tau_s X_c / X_s$, where τ_s is the lifetime of the solvated metal ion, and X_c and X_s are the corresponding mole fractions) in acetonitrile, methanol, dimethylformamide and pyridine. The magnitudes and temperature variations of τ_c are independent of the solvated Na^+ concentration in each set of $[NaL^1]^+$ solutions studied, as is seen from Fig. 2. This indicates that exchange occurs predominantly through a monomolecular decomplexation mechanism (eqn. (1)) where the decomplexation rate constant, $k_d = 1/\tau_c = k_c/K$, and k_c is the complexation rate constant. (The respective $[Na^+_{solvated}]$ and $[NaL^{1+}]$ in mol dm^{-3} in acetonitrile solutions (i)–(iv) are: 0.0750 and 0.0278, 0.0617 and 0.0411, 0.0442 and 0.0586, 0.0218 and 0.0810; in methanol solutions (i)–(iii): 0.0720 and 0.0309, 0.0463 and 0.0566, 0.0329 and 0.0700; in dimethylformamide solutions (i)–(iii): 0.0775 and 0.0245, 0.0581 and 0.0439, 0.0326 and 0.0694;

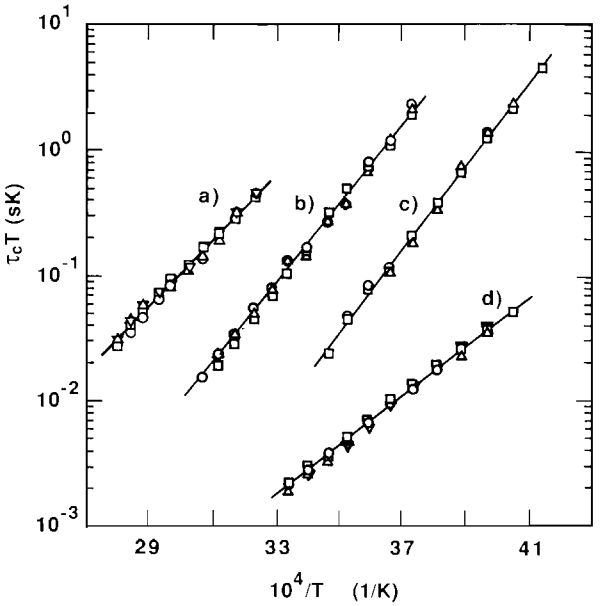

Fig. 2. The temperature variation of $T\tau_c$ for the $Na^+/[NaL^1]^+$ system in (a) pyridine, (b) methanol, (c) dimethylformamide and (d) acetonitrile ($T\tau_c/50$ in the last case). For pyridine and acetonitrile, the data points for solutions (i)–(iv) are represented by triangles, circles, squares and inverted triangles, respectively. For methanol and dimethylformamide, the data points for solutions (i)–(iii) are represented by triangles, circles and squares, respectively. Solution compositions are given in the text. The solid lines represent the best fits of the combined data for each group of solutions to the Eyring equation.

in pyridine solutions (i)–(iv): 0.0764 and 0.0282, 0.0638 and 0.0408, 0.0408 and 0.0638, 0.0253 and 0.0793.) The decomplexation activation parameters (Table 2) are derived from the temperature variation of k_d through the Eyring equation. The exchange of Na^+ is in the fast exchange limit in propylene carbonate, as is also the case for the exchange of Li^+ on $[LiL^1]^+$ in all five solvents.

$$Na^+ + L^1 \underset{k_d}{\overset{k_c}{\rightleftharpoons}} [NaL^1]^+ \qquad (1)$$

The fastest step in the complexation of Na^+ by L^1 is the diffusion controlled formation of an encounter complex in which Na^+ retains its first solvation shell in contact with L^1 [1]. In subsequent steps, desolvation, Na^+ binding and L^1 conformational changes occur culminating in the formation of $[NaL^1]^+$. The decomplexation of $[NaL^1]^+$ 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. Thus, k_c is a composite rate constant incorporating the slowest first order complexation step and the stability constant for the encounter complex. Our ^{23}Na NMR data quantify, but do not identify, the slowest decomplexation step. However, the sequential nature of such complexation processes has been demonstrated by ultrasonic relaxation studies of the complexation of Na^+ in related systems [18, 19].

The data in Table 2 are consistent with the involvement of a pendant arm in the rate determining steps as k_c and k_d differ significantly for $[NaL^1]^+$ and $[NaL^3]^+$ (as do the corresponding $\Delta H_d^{\neq}$ and $\Delta S_d^{\neq}$ magnitudes) where the methoxyethyl pendant arms of the former are replaced by hydroxyethyl pendant arms in the latter. The differing labilities of $[NaL^2]^+$ and $[NaL^4]^+$ and their Li^+ analogues similarly indicate pendant arm involvement in the slowest complexation step [1]. The observation that k_c and k_d are 11.7 and 21.4, and 3.9 and 5.6 times greater for $[NaL^1]^+$ than for $[NaL^2]^+$ in acetonitrile and pyridine, respectively, is consistent with the larger and more flexible L^1 labilizing the complexation and decomplexation processes to similar extents in a given solvent by comparison with those of L^2 while conferring a stability on $[NaL^1]^+$ similar to that of $[NaL^2]^+$. Variations of 4070 and 75 fold in k_c and k_d, respectively, are encompassed by the data obtained in acetonitrile, methanol, dimethylformamide and pyridine consistent with k_c dominating the variation of the stability of $[NaL^1]^+$ with change in solvent, and a similar situation exists for $[NaL^2]^+$. Thus, the rate

TABLE 2. Kinetic parameters for Na^+ exchange on $[NaL^n]^+$

$[NaL^n]^+$	Solvent	D_N	$10^{-5}k_c$ (298.2 K)[a] ($dm^3\ mol^{-1}\ s^{-1}$)	k_d (298.2 K) (s^{-1})	$\Delta H_d^{\neq}$ ($kJ\ mol^{-1}$)	$\Delta S_d^{\neq}$ ($J\ K^{-1}\ mol^{-1}$)
$[NaL^1]^+$ [b]	acetonitrile	14.1[c]	2154000	2650	37.5	−53.8
$[NaL^1]^+$ [b]	methanol	23.5[d]	903	2430	59.9	20.8
$[NaL^1]^+$ [b]	dimethylformamide	26.6[c]	529	25900	61.7	46.4
$[NaL^1]^+$ [b]	pyridine	33.1[c]	12300	347	50.9	−26.5
$[NaL^2]^+$ [e]	acetonitrile	14.1[c]	183400	124	43.2	−60.0
$[NaL^2]^+$ [e]	propylene carbonate	15.1[c]	7554	60.0	53.4	−32.0
$[NaL^2]^+$ [e]	pyridine	33.1[c]	3170	61.8	55.8	−23.5
$[NaL^3]^+$ [f]	methanol	23.5[d]	3058	4130	42.8	−32.0
$[NaL^4]^+$ [f]	acetonitrile	14.1[c]	20700	207	52.6	−24.1

[a] $k_c = k_d K$. [b] This work. [c] Ref. 7. [d] Ref. 8. [e] Ref. 2. [f] Ref. 1.

determining complexation and decomplexation steps both involve participation of solvent.

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