AN EQUILIBRIUM AND KINETIC STUDY OF THE COMPLEXATION OF LITHIUM AND SODIUM IONS BY THE CRYPTAND 4,7,13-TRIOXA-1,10-DIAZABICYCLO-[8.5.5]-EICOSANE (C21C₅).

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ABSTRACT. In the solid and solution state Li⁺ and Na⁺ form inclusive and exclusive cryptates respectively with C21C₅, in which Li⁺ resides inside and Na⁺ resides outside the C21C₅ cavity. Similar inclusive and exclusive structures are observed for [Li.C211]⁺ and [Na.C211]⁺. The logarithms of the stability constants in dimethylformamide for [Li.C21C₅]⁺, [Li.C211]⁺, [Na.C21C₅]⁺ and [Na.C211]⁺ are: 2.80, 6.99, 2.87 and 5.20; and the corresponding decomplexation rate constants are: 107, 0.013, 28800 and 12 s⁻¹ at 298.2 K. The relationships between cryptate structure, stability and lability are considered, as are solvent influences.

INTRODUCTION

In the solid state the cryptates [Na.C21C₅.NCS] and [Na.C211.NCS] exist in the exclusive form in which Na⁺ resides outside the cryptand cavity adjacent to the fifteen membered 4,7,13-trioxa-1,10-diaza ring;¹ and [Li.C21C₅]NCS² and [Li.C211]I³ exist in the inclusive form in which Li⁺ resides inside the cryptand cavity. ¹³C nmr studies indicate that [Na.C21C₅]⁺ and [Na.C211]⁺ (NCS⁻ within bonding distance of Na⁺ in the solid state is substantially displaced by solvent in solution) exist in the exclusive form; and [Li.C21C₅]⁺ and [Li.C211]⁺ exist in the inclusive form in solution.^{1,2} (The existence of the exclusive and inclusive cryptates is a consequence of the ionic diameters of Na⁺ and Li⁺, 2.04 Å and 1.52 Å respectively, being larger than and similar to the C21C₅ and C211 cavities of diameter 1.6 Å.) Cryptand C21C₅ has one less oxygen than C211:



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but is otherwise structurally similar, and thus affords an opportunity to study the effect of this difference on the stability and lability of the corresponding alkali metal cryptates.

RESULTS

The stability constant $(K_s = k_f/k_d)$, and formation (k_f) and decomplexation (k_d) rate constants characterizing the equilibrium:

$$M^{+} + C21C_{5} \xleftarrow{k_{f}} [M.C21C_{5}]^{+}$$
(1)

where $M^+ = Li^+$ or Na^+ , are related to the lifetimes of M^+ in the cryptate (T_C) and the solvated state (T_S) through eqns (2) and (3), where X_C and X_S are the mole fractions of M^+ in the cryptate and solvated state respectively, and all other symbols have their usual meanings.

$$\tau_C / X_C = \tau_S / X_C \tag{2}$$

$$1/\tau_{c} = k_{d} = (k_{B}T/h) \exp(-\Delta H^{\#}/RT + \Delta S^{\#}/R)$$
(3)

The K_S values for $[\text{Li.C21C}_5]^+$ and $[\text{Na.C21C}_5]^+$ were determined by ⁷Li nmr and potentiometric methods respectively; and the rates of Li⁺ and Na⁺ exchange were determined by nmr complete lineshape methods. An example of the coalescence of the ²³Na resonances arising from solvated Na⁺ and $[\text{Na.C21C}_5]^+$ as the temperature increases is shown in Figure 1. For both $[\text{Li.C21C}_5]^+$ and $[\text{Na.C21C}_5]^+$, and their C211 analogues,⁴,⁵ k_d is independent of concentration in a range of solvents and hence the dominant cryptate decomplexation process does not involve solvated M⁺ in the transition state.

Cryptate stability and lability vary substantially with the nature of M⁺ and cryptand as is exemplified by the data obtained in dimethyl-formamide shown in Table 1. It is also found that cryptate stability and lability are considerably affected by the nature of the solvent as is exemplified by the [Na.C21C₅]⁺ data in Table 2.

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cryptate	$10^{-3} k_{\rm f}/dm^{3} mol^{-1} s^{-1}$	k _d / s ⁻¹	log K _S /dm ³ mol ⁻¹	
$a_{[Li.C21C_5]}^+$	67	107	2.80	
b[Li.C211]+	127	0.013	6.99	
$a[Na.C21C_5]^+$	21400	28800	2.87	
<pre>(exclusive) c[Na.C211]+ (ma.lensive)</pre>	1920	12	5.20	
(exclusive) a This work;	^b Ref. 4; ^C Ref.	5.		

TABLE 1. Rate and apparent stability constants for cryptate systems in dimethylformamide solution at 298.2 K.



Figure 1. Typical exchange modified 79.39 MHz 23 Na nmr spectra of a dimethylformamide solution of NaClO₄ (0.106 mol dm⁻³) and C21C₅ (0.053 mol dm⁻³). Experimental temperatures and spectra appear at the left of the Figure and best fit calculated lineshapes and the corresponding τ_c values appear at the right. (A total of ten spectra at different temperatures were analysed for this solution.) The resonance of [Na.C21C₅]⁺ appears downfield of the resonance of solvated Na⁺.

DISCUSSION

The much higher stabilities of [Li.C211] + and [Na.C211] +, by comparison with those of $[Li.C21C_5]^+$ and $[Na.C21C_5]^+$ (Table 1), demonstrate the considerable importance of the fourth oxygen of C211 in rendering its cryptates substantially more stable than the C21C5 cryptates irrespective of their exclusive or inclusive structure. The greater stability of $[Li.C211]^+$ by comparison with that of $[Li.C21C_5]^+$ is largely a consequence of the greater k_d of the latter cryptate; and similarly the greater stability of [Na.C211] + by comparison with that of $[Na.C21C_5]^+$ is largely a consequence of the greater k_d of the latter cryptate (Table 1). This suggests that the rate determining step controlling the magnitude of k_d for [M.C211]⁺ involves the disruption of the interaction between the fourth oxygen of C211 and M^+ , while the absence of this interaction in $[M.C21C_5]^+$ results in greater k_d values. (A structural manifestation of these interaction differences is observed in the solid state where Na^+ is 0.14 Å and 0.37 Å above the face of the O_3 plane of the 4,7,10-trioxa-1,10-diaza ring to which it is bound in

Solvent	D_N^{b}	log K _S /dm ³ mol ⁻¹ (298.2 K)	10 ⁻⁵ kf dm ³ mol ⁻¹ s ⁻¹ (298.2 K)	kd s ⁻¹ (298.2 K)	∆Hd [#] kJ mol ⁻¹	$\frac{\Delta Sd^{\#}}{J K^{-1} mol^{-1}}$
aceto- nitrile	14.1	5.08	100	84.8±1.6	57.9±0.7	-13.8±2.1
propylene carbonate	15.1	5.12	25.5	19.4±0.5	70.3±0.5	15.3±1.4
acetone	17.0	3.98	84	878±6	54.4±0.4	-6.1±1.2
methanol	19.0	3.76	104	1800±50	44.9±0.1	-31.9±0.4
dimethyl- formamide	26.6	2.87	214	28800±300	40.0±0.1	-25.3±0.5
pyridine	33.1	3.72	4.9	93.5±0.5	62.8±0.2	3.3±0.5

Table 2. Parameters^a for [Na.C21C₅]⁺ in various solvents

^a Quoted errors represent one standard deviation obtained from a linear regression analysis of the temperature dependence of experimental τ_c data through eqn 3.

^b Gutmann donor number from ref. 6. The dielectric constants from the same reference are: acetonitrile 38.0, propylene carbonate 69.0, acetone 20.7, methanol 32.6, dimethylformamide 36.1, dimethyl sulfoxide 45.0, and pyridine 12.3. It should be noted that other authors have used D_N values for some solvents which differ from those originally derived by Gutmann - e.g. B.O. Strasser and A.I. Popov, J.Am.Chem.Soc., 1985 107, 7921.

[Na.C211.NCS] and [Na.C21C5.NCS] respectively.¹)

Exclusive $[Na.C21C_5]^+$ is characterized by larger k_f and k_d values than inclusive $[Li.C21C_5]^+$, which probably indicates that for the latter cryptate these rate constants are largely determined by entry to, and exit from the C21C₅ cavity. Thus Li⁺ exchange between the solvated and inclusive cryptate environments is envisaged to proceed through a reactive exclusive intermediate as shown in the two major steps:

$$Li^{+} + C21C_{5} \xleftarrow{\text{Last}} [Li.C21C_{5}]^{+} \xleftarrow{\text{Slow}} [Li.C21C_{5}]^{+} (4)$$
(exclusive) (inclusive)

In contrast Na⁺ exchange between the solvated and exclusive cryptate environments proceeds through a single major step:

$$Na^{+} + C21C_{5} \xleftarrow{\kappa_{f}}_{k_{d}} [Na.C21C_{5}]^{+}$$
(5)

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Corresponding mechanisms are envisaged for M⁺ exchange on [M.C211]⁺.

The data in Table 2 show that K_S characterizing equilibrium (5) is solvent dependent largely due to the variation of kd. This variation appears to depend on the electron donating power of the solvent, as expressed through the Gutmann donor number (D_N) ,⁶ and the steric characteristics of the solvent. Thus as D_N increases in the sequence: acetonitrile < acetone < methanol < dimethylformamide, kd increases, which suggests that the ability of solvent to compete with C21C₅ for bonding sites on Na⁺ in [Na.C21C₅]⁺ is important in the rate determining decomplexation step. On this basis it appears that the lower than expected kd values observed for propylene carbonate and pyridine may be a consequence of their effective electron donating abilities being decreased, below that expected from their D_N values, due to their bulkiness preventing a close approach to the sterically crowded Na⁺ in [Na.C21C₅]⁺. There is no apparent correlation between kd and solvent dielectric constant (Table 2).

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