

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).

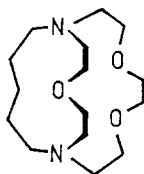
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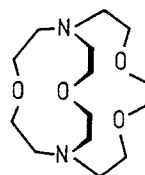
ABSTRACT. In the solid and solution state Li⁺ and Na⁺ form inclusive and exclusive cryptates respectively with C21C₅, in which Li⁺ resides inside and Na⁺ resides outside the C21C₅ cavity. Similar inclusive and exclusive structures are observed for [Li.C211]⁺ and [Na.C211]⁺. The logarithms of the stability 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:



C21C₅

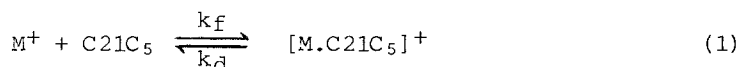


C211

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:



where $M^+ = Li^+$ or Na^+ , are related to the lifetimes of M^+ in the cryptate (τ_C) and the solvated state (τ_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.

$$\tau_C/X_C = \tau_S/X_S \quad (2)$$

$$1/\tau_C = k_d = (k_B T/h) \exp(-\Delta H^\ddagger/RT + \Delta S^\ddagger/R) \quad (3)$$

The K_S values for $[Li.C21C_5]^+$ and $[Na.C21C_5]^+$ 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 ^{23}Na resonances arising from solvated Na^+ and $[Na.C21C_5]^+$ as the temperature increases is shown in Figure 1. For both $[Li.C21C_5]^+$ and $[Na.C21C_5]^+$, 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 dimethylformamide 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 $[Na.C21C_5]^+$ data in Table 2.

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

cryptate	$10^{-3}k_f/$ $dm^3 mol^{-1} s^{-1}$	$k_d/$ s^{-1}	\log $K_S/dm^3 mol^{-1}$
^a $[Li.C21C_5]^+$ (inclusive)	67	107	2.80
^b $[Li.C211]^+$ (inclusive)	127	0.013	6.99
^a $[Na.C21C_5]^+$ (exclusive)	21400	28800	2.87
^c $[Na.C211]^+$ (exclusive)	1920	12	5.20

^a This work; ^b Ref. 4; ^c Ref. 5.

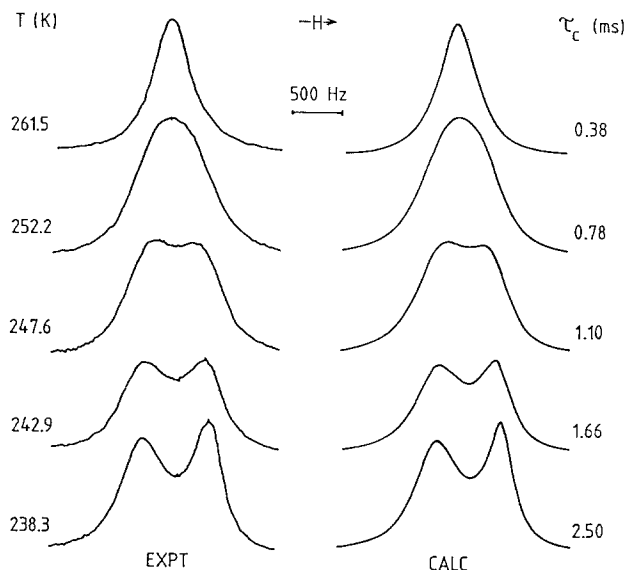


Figure 1. Typical exchange modified 79.39 MHz ^{23}Na nmr spectra of a dimethylformamide solution of NaClO_4 ($0.106 \text{ mol dm}^{-3}$) and $\text{C}21\text{C}_5$ ($0.053 \text{ mol dm}^{-3}$). Experimental temperatures and spectra appear at the left of the Figure and best fit calculated lineshapes 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 $[\text{Na.C}21\text{C}_5]^+$ appears downfield of the resonance of solvated Na^+ .

DISCUSSION

The much higher stabilities of $[\text{Li.C}211]^+$ and $[\text{Na.C}211]^+$, by comparison with those of $[\text{Li.C}21\text{C}_5]^+$ and $[\text{Na.C}21\text{C}_5]^+$ (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 $[\text{Li.C}211]^+$ by comparison with that of $[\text{Li.C}21\text{C}_5]^+$ is largely a consequence of the greater k_d of the latter cryptate; and similarly the greater stability of $[\text{Na.C}211]^+$ by comparison with that of $[\text{Na.C}21\text{C}_5]^+$ 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 $[\text{M.C}211]^+$ involves the disruption of the interaction between the fourth oxygen of C211 and M^+ , while the absence of this interaction in $[\text{M.C}21\text{C}_5]^+$ 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 O₃ plane of the 4,7,10-trioxa-1,10-diaza ring to which it is bound in

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 k_d . 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, k_d increases, which suggests that the ability of solvent to compete with C21C₅ for bonding sites on Na^+ in $[Na.C21C_5]^+$ is important in the rate determining decomplexation step. On this basis it appears that the lower than expected k_d 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 $[Na.C21C_5]^+$. There is no apparent correlation between k_d and solvent dielectric constant (Table 2).

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