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).


#### Abstract

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ABSTRACT. In the solid and solution state $\mathrm{Li}^{+}$and $\mathrm{Na}^{+}$form inclusive and exclusive cryptates respectively with $\mathrm{C}_{2} 1 \mathrm{C}_{5}$, in which $\mathrm{Li}{ }^{+}$resides inside and $\mathrm{Na}^{+}$resides outside the $\mathrm{C}_{2} 1 \mathrm{C}_{5}$ cavity. Similar inclusive and exclusive structures are observed for [Li.C211] ${ }^{+}$and [Na.C211] ${ }^{+}$. The logarithms of the stability constants in dimethylformamide for $\left[\mathrm{Li} . \mathrm{C} 21 \mathrm{C}_{5}\right]^{+},[\mathrm{Li} . \mathrm{C} 211]^{+},\left[\mathrm{Na.C21C}_{5}\right]^{+}$and $[\mathrm{Na} . \mathrm{C} 211]^{+}$are: $2.80,6.99$, 2.87 and 5.20; and the corresponding decomplexation rate constants are: 107, $0.013,28800$ and $12 \mathrm{~s}^{-1}$ 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.C21C 5 .NCS] and [Na.C211.NCS] exist in the exclusive form in which $\mathrm{Na}^{+}$resides outside the cryptand cavity adjacent to the fifteen membered 4,7,13-trioxa-1,10-diaza ring; ${ }^{1}$ and [Li.C21C5]NCS ${ }^{2}$ and [Li.C211]I ${ }^{3}$ exist in the inclusive form in which Li+ resides inside the cryptand cavity. ${ }^{13} \mathrm{C} \mathrm{nmr}$ studies indicate that [Na.C21C5] ${ }^{+}$and [Na.C211] ${ }^{+}$(NCS ${ }^{-}$within bonding distance of $\mathrm{Na}^{+}$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 $\mathrm{Na}^{+}$and $L_{i}{ }^{+}, 2.04 \AA$ and $1.52 \AA$ respectively, being larger than and similar to the $\mathrm{C} 21 \mathrm{C}_{5}$ and C211 cavities of diameter 1.6 A.) Cryptand $\mathrm{C} 21 \mathrm{C}_{5}$ has one less oxygen than C211:

$\mathrm{C}_{21} \mathrm{C}_{5}$


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 ( $\mathrm{K}_{\mathrm{S}}=\mathrm{k}_{\mathrm{f}} / \mathrm{k}_{\mathrm{d}}$ ), and formation ( $\mathrm{k}_{\mathrm{f}}$ ) and decomplexation ( $k d$ ) rate constants characterizing the equilibrium:

$$
\begin{equation*}
M^{+}+C 21 C_{5} \underset{k_{d}}{\stackrel{k_{f}}{\rightleftharpoons}}\left[M . C 21 C_{5}\right]^{+} \tag{1}
\end{equation*}
$$

where $\mathrm{M}^{+}=\mathrm{Li}{ }^{+}$or $\mathrm{Na}^{+}$, are related to the lifetimes of $\mathrm{M}^{+}$in the cryptate ( $\mathrm{T}_{\mathrm{C}}$ ) and the solvated state ( $\mathrm{T}_{\mathrm{s}}$ ) 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.

$$
\begin{align*}
& \tau_{\mathrm{C}} / \mathrm{X}_{\mathrm{C}}=\mathrm{T}_{\mathrm{s}} / \mathrm{X}_{\mathrm{C}}  \tag{2}\\
& 1 / \tau_{\mathrm{C}}=\mathrm{k}_{\mathrm{d}}=\left(\mathrm{k}_{\mathrm{B}} T / \mathrm{h}\right) \exp \left(-\Delta \mathrm{H}^{\#} / \mathrm{RT}+\Delta \mathrm{S}^{\# / R}\right) \tag{3}
\end{align*}
$$

The $\mathrm{K}_{\mathrm{S}}$ values for $\left[\mathrm{LI}_{\mathrm{i}} \mathrm{C} 21 \mathrm{C}_{5}\right]^{+}$and $\left[\mathrm{Na} . \mathrm{C} 21 \mathrm{C}_{5}\right]^{+}$were determined by ${ }^{7} \mathrm{Li}$ $n m r$ and potentiometric methods respectively; and the rates of Li+ and $\mathrm{Na}^{+}$exchange were determined by nmr complete lineshape methods. An example of the coalescence of the ${ }^{23} \mathrm{Na}$ resonances arising from solvated $\mathrm{Na}^{+}$and $\left[\mathrm{Na} . \mathrm{C} 21 \mathrm{C}_{5}\right]^{+}$as the temperature increases is shown in Figure 1. For both [Li.C21C $]_{5}{ }^{+}$and $\left[\mathrm{Na} . \mathrm{C} 21 \mathrm{C}_{5}\right]^{+}$, and their C211 analogues, ${ }^{4},{ }^{5} \mathrm{k}_{\mathrm{d}}$ is independent of concentration in a range of solvents and hence the dominant cryptate decomplexation process does not involve solvated $\mathrm{M}^{+}$ in the transition state.

Cryptate stability and lability vary substantially with the nature of $\mathrm{M}^{+}$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.C21C5] ${ }^{+}$data in Table 2.

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

| cryptate | $\frac{{ }^{10^{-3}} \mathrm{kff}^{\mathrm{f}} /}{\mathrm{mol}^{-1}} \mathrm{~s}^{-1}$ | $\begin{aligned} & k_{d} / \\ & s^{-1} \end{aligned}$ | $\begin{gathered} \log \\ \mathrm{K}_{\mathrm{s}} / \mathrm{dm}^{3} \mathrm{~mol}^{-1} \end{gathered}$ |
| :---: | :---: | :---: | :---: |
| $\left.a_{[\text {Li. }} 21 \mathrm{C}_{5}\right]^{+}$ | 67 | 107 | 2.80 |
| ${ }_{\text {(inclusive) }}{ }_{\text {[Li.C211] }}{ }^{\text {( }}$ | 127 | 0.013 | 6.99 |
| (inclusive) <br> $\mathrm{a}_{\left[\mathrm{Na} . \mathrm{C} 21 \mathrm{C}_{5}\right]+}{ }^{+}$ <br> (exclusive) | 21400 | 28800 | 2.87 |
| $\begin{aligned} & \mathrm{C}[\mathrm{Na.C} 211]^{+} \\ & \text {(exclusive) } \end{aligned}$ | 1920 | 12 | 5.20 |
| a This work; | 4; C R |  |  |



Figure 1. Typical exchange modified $79.39 \mathrm{MHz}{ }^{2}{ }^{3} \mathrm{Na} \mathrm{nmr}$ spectra of a dimethylformamide solution of $\mathrm{NaClO}_{4}\left(0.106 \mathrm{~mol} \mathrm{dm}{ }^{-3}\right)$ and $\mathrm{C} 21 \mathrm{C}_{5}(0.053$ mol $\mathrm{dm}^{-3}$ ). Experimental temperatures and spectra appear at the left of the Figure and best fit calculated lineshapes and the corresponding $\tau_{C}$ values appear at the right. (A total of ten spectra at different temperatures were analysed for this solution.) The resonance of $\left[\mathrm{Na} . \mathrm{C} 21 \mathrm{C}_{5}\right]^{+}$appears downfield of the resonance of solvated $\mathrm{Na}^{+}$.

## DISCUSSION

The much higher stabilities of [Li.C211] ${ }^{+}$and [Na.C211] ${ }^{+}$, by comparison with those of [Li.C21C55] and [Na.C21C $\left.{ }_{5}\right]^{+}$(Table 1), demonstrate the considerable importance of the fourth oxygen of c211 in rendering its cryptates substantially more stable than the $C 21 C_{5}$ cryptates irrespective of their exclusive or inclusive structure. The greater stability of [Li.C211] ${ }^{+}$by comparison with that of [Li.C21C $]^{+}{ }^{+}$is largely a consequence of the greater $\mathrm{k}_{\mathrm{d}}$ of the latter cryptate; and similarly the greater stability of [Na.C211] ${ }^{+}$by comparison with that of $\left[\mathrm{Na} . \mathrm{C} 21 \mathrm{C}_{5}\right]^{+}$is largely a consequence of the greater $\mathrm{k}_{\mathrm{d}}$ of the latter cryptate (Table 1). This suggests that the rate determining step controlling the magnitude of $\mathrm{k}_{\mathrm{d}}$ for $[\mathrm{M} . \mathrm{C} 211]^{+}$involves the disruption of the interaction between the fourth oxygen of C 211 and $\mathrm{M}^{+}$, while the absence of this interaction in [M.C21C5] ${ }^{+}$results in greater $\mathrm{k}_{\mathrm{d}}$ values. (A structural manifestation of these interaction differences is observed in the solid state where $\mathrm{Na}^{+}$is $0.14 \AA$ and $0.37 \AA$ above the face of the $O_{3}$ plane of the 4,7,10-trioxa-1,10-diaza ring to which it is bound in

Table 2. Parameters ${ }^{\text {a }}$ for $\left[\mathrm{Na.C} 21 \mathrm{C}_{5}\right]^{+}$in various solvents

| Solvent | $\mathrm{D}_{\mathrm{N}}{ }^{\text {b }}$ | $\begin{gathered} \log \\ \mathrm{K}_{\mathrm{S}} / \mathrm{dm}^{3} \mathrm{~mol}^{-1} \\ (298.2 \mathrm{~K}) \end{gathered}$ | $\begin{gathered} 10^{-5} \mathrm{kff}^{\mathrm{c}} \\ \mathrm{dm}^{3} \mathrm{~mol}^{-1} \mathrm{~s}^{-1} \\ (298.2 \mathrm{~K}) \end{gathered}$ | $\begin{gathered} \mathrm{k}_{\mathrm{d}} \\ \mathrm{~s}^{-1} \\ (298.2 \mathrm{~K}) \end{gathered}$ | $\begin{gathered} \Delta \mathrm{Hd}^{\#} \\ \mathrm{~kJ} \mathrm{~mol}^{-1} \end{gathered}$ | $\mathrm{J} \mathrm{~K}^{-1} \mathrm{SO}_{\mathrm{d}} \mathrm{~mol}^{-1}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| acetonitrile | 14.1 | 5.08 | 100 | $84.8 \pm 1.6$ | $57.9 \pm 0.7$ | $-13.8 \pm 2.1$ |
| propylene carbonate | 15.1 | 5.12 | 25.5 | $19.4 \pm 0.5$ | $70.3 \pm 0.5$ | $15.3 \pm 1.4$ |
| acetone | 17.0 | 3.98 | 84 | $878 \pm 6$ | $54.4 \pm 0.4$ | $-6.1 \pm 1.2$ |
| methanol | 19.0 | 3.76 | 104 | $1800 \pm 50$ | $44.9 \pm 0.1$ | $-31.9 \pm 0.4$ |
| dimethyl- <br> formamide | 26.6 | 2.87 | 214 | $28800 \pm 300$ | $40.0 \pm 0.1$ | $-25.3 \pm 0.5$ |
| pyridine | 33.1 | 3.72 | 4.9 | $93.5 \pm 0.5$ | $62.8 \pm 0.2$ | $3.3 \pm 0.5$ |

a Quoted errors represent one standard deviation obtained from a linear regression analysis of the temperature dependence of experimental $\tau_{C}$ 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.C21C5] ${ }^{+}$is characterized by larger $\mathrm{k}_{\mathrm{f}}$ and $\mathrm{k}_{\mathrm{d}}$ values than inclusive [ $\left.\mathrm{Li}_{\mathrm{i}} \mathrm{C} 21 \mathrm{C}_{5}\right]^{+}$, which probably indicates that for the latter cryptate these rate constants are largely determined by entry to, and exit from the $C 21 C_{5}$ 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:


In contrast $\mathrm{Na}^{+}$exchange between the solvated and exclusive cryptate environments proceeds through a single major step:

$$
\begin{equation*}
\mathrm{Na}^{+}+\mathrm{C} 21 \mathrm{C}_{5} \xlongequal[\mathrm{k}_{\mathrm{d}}]{\stackrel{\mathrm{k}_{\mathrm{f}}}{\rightleftharpoons}} \underset{\text { (exclusive) }}{\left[\mathrm{Na} . \mathrm{C} 21 \mathrm{C}_{5}\right]}+ \tag{5}
\end{equation*}
$$

Corresponding mechanisms are envisaged for $\mathrm{M}^{+}$exchange on [M.C211] ${ }^{+}$.
The data in Table 2 show that $\mathrm{K}_{\mathrm{S}}$ characterizing equilibrium (5) is solvent dependent largely due to the variation of $\mathrm{k}_{\mathrm{d}}$. This variation appears to depend on the electron donating power of the solvent, as expressed through the Gutmann donor number ( $\mathrm{D}_{\mathrm{N}}$ ), ${ }^{6}$ and the steric characteristics of the solvent. Thus as $D_{N}$ increases in the sequence: acetonitrile < acetone < methanol < dimethylformamide, $\mathrm{k}_{\mathrm{d}}$ increases, which suggests that the ability of solvent to compete with C21C5 for bonding sites on $\mathrm{Na}^{+}$in $\left[\mathrm{Na} . \mathrm{C} 21 \mathrm{C}_{5}\right]^{+}$is important in the rate determining decomplexation step. On this basis it appears that the lower than expected $\mathrm{k}_{\mathrm{d}}$ 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 theix bulkiness preventing a close approach to the sterically crowded $\mathrm{Na}^{+}$in [Na.C21C5] ${ }^{+}$. There is no apparent correlation between $\mathrm{k}_{\mathrm{d}}$ and solvent dielectric constant (Table 2).

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