Inorganica Chimica Acta, *190* (1991) 223–229

Complexation of lithium(I), sodium(I), silver(I) and thallium(I) by 4,7,13,16-tetraoxa-1,10-diazabicyclo[8.5.5]eicosane and 4,7,13-trioxa-1,10-diazabicyclo[8.5.5]eicosane in trimethyl phosphate. A potentiometric titration and ^{7}Li and ^{23}Na nuclear magnetic resonance study

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(Received June 11, 1991; revised September 2, 1991)

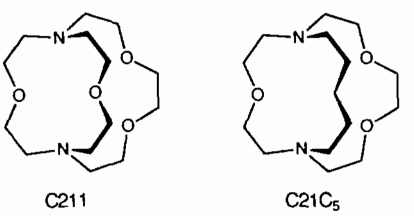
Abstract

Complexation of $M^+ = Li^+$, Na^+, Ag^+ and Tl^+ by the cryptands 4,7,13,18-tetraoxa-1,10-diazabicyclo[8.5.5]eicosane (C211) and 4,7,13-trioxa-1,10-diazabicyclo[8.5.5]eicosane (C21C$_5$) to form the cryptates $[M.C211]^+$ and $[M.C21C_5]^+$ has been studied in trimethyl phosphate by potentiometric titration and ^{7}Li and ^{23}Na NMR spectroscopy. For $[M.C211]^+$ the logarithm of the apparent stability constants, $\log K$ (dm^3 mol^{-1})$=6.98\pm0.05$, 5.38 ± 0.05, 9.82 ± 0.02 and 3.95 ± 0.02 for $M^+ = Li^+$, Na^+, Ag^+ and Tl^+, respectively; and for $[M.C21C_5]^+$ $\log K$ (dm^3 mol^{-1})$=2.40\pm0.10$, 1.90 ± 0.05, 6.04 ± 0.02 and 2.42 ± 0.10 for $M^+ = Li^+$, Na^+, Ag^+ and Tl^+, respectively. The decomplexation kinetic parameters for $[Na.C211]^+$ are: k_d (298.2 K)$=6.92\pm0.50$ s^{-1}, $\Delta H_d^{\neq}=62.2\pm0.9$ kJ mol^{-1}, and $\Delta S_d^{\neq}=-20.3\pm2.7$ J K^{-1} mol^{-1}; and those for $[Li.C21C_5]^+$ are: k_d (298.2 K)$=23.3\pm0.4$ s^{-1}, $\Delta H_d^{\neq}=61.2\pm1.1$ kJ mol^{-1}, and $\Delta S_d^{\neq}=-13.6\pm3.6$ J K^{-1} mol^{-1}. Metal ion exchange on $[Li.C211]^+$ is in the very slow extreme of the NMR timescale up to 390 K and $k_d \ll 4$ s^{-1} at 298.2 K, while in contrast exchange on $[Na.C21C_5]^+$ is in the fast extreme of the NMR timescale at 298.2 K ($k_d \approx 10^4$ s^{-1}). These data are compared with those obtained in other solvents.

Introduction

The stability and lability of the metal complexes, or cryptates, formed by polyoxadiazabicycloalkanes, or cryptands, are dependent on the structure of the cryptand the number and type of its donor atoms, and the natures of the metal ion and the solvent [1–18]. In this study we examine several of these aspects through the cryptates formed by 4,7,13,18-tetraoxa-1,10-diazabicyclo[8.5.5]eicosane (C211) and 4,7,13-trioxa-1,10-diazabicyclo[8.5.5]eicosane (C21C$_5$) where the cryptands have cavities of similar size, but the first cryptand has one more oxygen donor atom (Fig. 1) and affords an opportunity to examine the effect of the number of cryptand donor atoms on the characteristics of the cryptates of Li^+, Na^+, Ag^+ and Tl^+ in trimethyl phosphate solvent. The selection of Li^+ and Na^+ is a consequence of the crystal structures of the cryptates $[Li.C211]^+$ and $[Li.C21C_5]^+$, and their Na^+ analogues [19–21] being available to provide a basis for discussion of their solution properties. In addition ^{7}Li and ^{23}Na have good NMR sensitivity which facilitates NMR kinetic studies of these cryptates. The soft acid characteristics of Ag^+ and Tl^+ provide a contrast with the hard acid character of Li^+ and Na^+ [22, 23].

Trimethyl phosphate has been selected as the solvent to extend the data available on the influence of the solvent on cryptate chemistry. Cryptate stability tends to decrease with increase in the electron doning ability of the solvent as indicated by the Gutmann donor number, D_N [24–26]. However, in the case of water two D_N values, 18.0 and 33.0, are quoted, and in the case of methanol D_N values of 19.0 and 23.5 are quoted [25, 26]. (In each case the first value is that obtained in dilute solutions of the protic solvent



C211 C21C$_5$

Fig. 1. Structures of the cryptands C211 and C21C$_5$.

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in 1,2-dichloroethane solution, and the second value is that obtained when the protic solvent is the bulk solvent). Apparent anomalies in alkali metal ion cryptate stability and lability variations with the nature of the solvent which arise when the first D_N values are used are largely removed when the second values are used, and it has been argued that this may be because the second value reflects the hydrogen bonded character of the protic solvents which becomes important when they are the bulk solvent [8, 9, 18]. On this basis the second D_N values may more effectively reflect the electron doning power of the protic solvents when they are the bulk solvent. Nevertheless, it is desirable to test this assertion by selecting an aprotic solvent with a D_N value as close as possible to the second value of the protic solvents. Accordingly, the solvent chosen for this study is trimethyl phosphate whose $D_N = 23.0$ is very close to the second methanol value, and which appears not to have been previously used as a solvent in cryptate studies.

Experimental

Materials

The cryptand $C21C_5$ was prepared as described previously [21] and C211 (Merck) was redistilled. Lithium and sodium perchlorate (Fluka) and silver nitrate (Merck) were vacuum dried at 353–363 K for 48 h and were stored over P_2O_5 under vacuum. Thallium perchlorate was prepared from Tl_2CO_3 and $HClO_4$ by metathesis in water, recrystallised twice from water and dried as described above. Trimethyl phosphate (BDH) was distilled and dried over Linde 4 Å molecular sieves. All solutions were prepared under dry nitrogen in a glove box.

Potentiometric Titrations

Stability constants for $[Na.C211]^+$ and $[Na.C21C_5]^+$ were determined by duplicated potentiometric titration of 25 cm^3 of 10^{-3} mol dm^{-3} $NaClO_4$ solutions with 10^{-2} mol dm^{-3} solutions of the appropriate cryptand. The titrations were carried out under dry nitrogen in a thermostatted (298.15 ± 0.01 K) titration vessel using a Radiometer G502 Na^+ specific electrode and an Ag wire reference electrode in a 10^{-2} mol dm^{-3} $AgNO_3$ solution in a thermostatted reference vessel (the two vessels were linked using a salt bridge containing 0.05 mol dm^{-3} Et_4NClO_4 solution) and an Orion Research SA 720 digital analyser. For all other titrations the Na^+ specific electrode was replaced by a silver wire electrode, but the equipment used was otherwise identical. Stability constants for $[Ag.C211]^+$ and $[Ag.C21C_5]^+$ were determined by duplicated potentiometric titrations of 25 cm^3 of 10^{-3} mol dm^{-3} $AgNO_3$ solution with 10^{-2} mol dm^{-3} C211 or $C21C_5$ solution. These data were employed in the derivation of the stability constants of $[Li.C211]^+$ and $[Li.C21C_5]^+$ from data obtained from a competitive potentiometric titration of 25 cm^3 of 10^{-3} mol dm^{-3} $AgNO_3$ solution with a solution 10^{-2} mol dm^{-3} in either C211 or $C21C_5$ and 5×10^{-2} mol dm^{-3} in $LiClO_4$ as described in the literature [10, 14]. The stability constant of $[Tl.C211]^+$ was obtained through a competitive potentiometric titration of 25 cm^3 of 10^{-3} mol dm^{-3} $AgNO_3$ solution with a solution 10^{-2} mol dm^{-3} in $C21C_5$ and 5×10^{-2} mol dm^{-3} in $TlClO_4$, while for $[Tl.C21C_5]^+$ the concentrations of the titration solutions were halved to accommodate the decreased solubility of this cryptate. All solutions were 0.05 mol dm^{-3} in Et_4NClO_4.

NMR spectroscopy

For variable temperature ^7Li and ^{23}Na NMR spectroscopic studies, solutions were sealed under vacuum in 5-mm NMR tubes and coaxially mounted in 10-mm NMR tubes containing either D_2O, d_6-acetone or d_6-dimethyl sulfoxide, which provided the lock signal. ^7Li NMR spectra were run on a Bruker CXP-300 spectrometer operating at 116.64 MHz. For each solution an average of 500 transients was accumulated in a 8192 point data base over a 1199 Hz spectral width for each solution prior to Fourier transformation. ^{23}Na NMR spectra were run at 79.39 MHz and an average of 1000 transients was accumulated in a 2048 data point base over a 8064.5 Hz spectral width for each solution prior to Fourier transformation. Spectra were collected at temperature intervals of *c.* 5 K and the solution temperatures were controlled to within ± 0.3 K using a Bruker B-VT 1000 temperature controller. The Fourier transformed spectra were subjected to complete lineshape analysis [27] on a VAX 11-780 computer to obtain kinetic data. The temperature dependent ^7Li and ^{23}Na linewidths and chemical shifts employed in the lineshape analysis were obtained from a combination of extrapolation from low temperatures where no exchange induced modification occurred, and from the linewidth and chemical shift variations of separate solutions containing Li^+ or Na^+ or one of their cryptates alone.

Results and discussion

Cryptate stabilities

In trimethyl phosphate the apparent stability constant, *K*, of the cryptate formed by C211, $[M.C211]^+$, varies considerably with the nature of M^+, and for a given M^+ a marked decrease in K is observed for $[M.C21C_5]^+$ by comparison with that characterizing $[M.C211]^+$ (Table 1). In the solid state $[Li.C21C_5]^+$ and $[Li.C211]^+$ exist as *inclusive* cryptates [19, 20], where Li^+ resides in the cryptand cavities consistent with an optimal fit of Li^+ ($r = 76$ pm [28]) into the C211 and $C21C_5$ cavities ($r \approx 80$ pm [1]). NMR studies indicate that $[Li.C211]^+$ largely retains its *inclusive* structure in solution [16], whereas $[Li.C21C_5]^+$ probably exists in a dynamic equilibrium between the *inclusive* and *exclusive* cryptates where in the latter case Li^+ is largely outside the cryptand cavity and adjacent to the fifteen membered ring of $C21C_5$ delineated by two nitrogens and three oxygens [9]. Such *exclusive* structures are observed for $[Na.C21C_5]^+$ and $[Na.C211]^+$ [21] in the solid state and reflect the larger size of Na^+ ($r = 102$ pm) which excludes it from entry into the cavities of either cryptand. On this basis the greater K observed for $[Li.C211]^+$, by comparison with that characterizing $[Na.C211]^+$, may be rationalised in terms of the optimal fit of Li^+ into the C211 cavity resulting in increased stability, and it is seen that this relative order of stability applies for the other solvents listed in Table 1. The magnitude of K for $[M.C21C_5]^+$ is considerably smaller than that for $[M.C211]^+$ consistent with the replacement of an ether oxygen atom by a methylene group resulting in a decreased electrostatic interaction between M^+ and $C21C_5$. The relative order of stability $[Li.C21C_5]^+ > [Na.C21C_5]^+$ holds in trimethyl phosphate solvent, but is reversed in the other solvents listed in Table 1 which may reflect the varying proportions of $[Li.C21C_5]^+$ existing in the *inclusive* and *exclusive* form and its consequent variation in overall stability relative to $[Na.C21C_5]^+$.

In trimethyl phosphate and other oxygen donor solvents $[Ag.C211]^+$ and $[Ag.C21C_5]^+$ are considerably more stable than their Li^+ and Na^+ analogues (Table 1) and this is attributable to the tendency of the soft acid Ag^+ to bond with nitrogen donor atoms preferentially [22, 23]. (Ag^+ also shows a tendency to form two strong bonds in linear array [29] which may be approximately accommodated here through bonding with the two cryptand nitrogens). Thus oxygen donor solvents do not compete as effectively with the cryptand for Ag^+ as they do for the hard acid Li^+ and Na^+ ions, and this contributes to the greater stability of the Ag^+ cryptates. However, in nitrogen donor acetonitrile the same argument explains the reversal in stability whereby the Li^+ and Na^+ cryptates become more stable than the Ag^+ cryptates.

In all of the solvents listed in Table 1 $[Tl.C211]^+$ is less stable than its Li^+, Na^+ and Ag^+ analogues,

TABLE 1. Apparent stability constants for cryptates formed by some monovalent metal ions and 4,7,13,18-tetraoxa-1,10-diazabicyclo[8.5.5]eicosane (C211) and 4,7,13-trioxa-1,10-diazabicyclo[8.5.5]eicosane ($C21C_5$) in various solvents at 298.2 K

Solvent	D_N	log K ($dm^3\ mol^{-1}$)			
		$[Li.C211]^+$	$[Na.C211]^+$	$[Ag.C211]^+$	$[Tl.C211]^+$
Acetonitrile	14.1[a]	> 10[b]	9.8[c] 8.74[e]	7.70[b] 7.74[e]	7.02[d]
Propylene carbonate	15.1[a]	12.44[b]	8.76[b]	14.44[b]	6.58[d]
Water	18.0[a] 33.0[g]	5.5[b]	3.2[f] 2.8[c]	8.5[b]	3.19[d]
Methanol	19.0[a] 23.5[g]	8.04[b]	6.7[c] 6.64[e]	10.60[b] 10.46[e]	5.65[d]
Trimethyl phosphate	23.0[a]	6.98 ± 0.05[h]	5.38 ± 0.05[h]	9.82 ± 0.02[h]	3.95 ± 0.02[h]
Dimethylformamide	26.6[a]	6.99[b] 6.73[b]	5.23[b] 5.10[b]	8.60[b] 8.62[b]	3.15[d]
Dimethylsulfoxide	29.8[a]	5.84[b]	4.63[b]	6.17[b]	1.44[d]
		$[Li.C21C_5]^+$	$[Na.C21C_5]^+$	$[Ag.C21C_5]^+$	$[Tl.C21C_5]^+$
Acetonitrile	14.1[a]	4.15[i]	5.08[j]	4.29[i]	
Methanol	19.0[a] 23.5[g]	3.00[i]	3.76[j]	7.69[i]	
Trimethyl phosphate	23.0[a]	2.40 ± 0.10[h]	1.90 ± 0.05[h]	6.04 ± 0.02[h]	2.42 ± 0.10[h]
Dimethylformamide	26.6[a]	1.80[i]	2.87[j]	5.23[i]	

[a] Ref. 24. [b] Ref. 6 and refs. therein. [c] Ref. 11. [d] Ref. 14 and refs. therein. [e] Ref. 12 and refs. therein. [f] Ref. 10. [g] Refs. 25 and 26. [h] This work. [i] Ref. 9. [j] Ref. 7.

except in water where its stability is comparable to that of $[Na.C211]^+$. This indicates that Tl^+ does not have as strong an interaction with cryptand nitrogen donor atoms as that exhibited by Ag^+ and that its relatively large size ($r = 150$ pm) decreases its interaction with the C211 oxygen atom in the $-(CH_2)_2O(CH_2)_2-$ moiety opposite the fifteen membered cryptand ring delineated by two nitrogens and three oxygens which Tl^+ is probably adjacent to in *exclusive* $[Tl.C211]^+$. (This assumption of an *exclusive* cryptate structure is based on the observation of the *exclusive* $[Na.C211]^+$ in the solid state [21] ($r = 102$ pm for Na^+), which indicates that $[Ag.C211]^+$ may also exist in the *exclusive* form ($r = 115$ pm for Ag^+).) In trimethyl phosphate the stability of $[Tl.C21C_5]^+$ is similar to that of its Li^+ and Na^+ analogues which may reflect that the advantage arising from the smaller sizes of the latter two ions in the close approach to the six donor atoms of C211 is lost in $C21C_5$ where all five donor atoms are disposed around one fifteen membered cryptand ring.

A comparison of the K values observed for $[M.C211]^+$ and $[M.C21C_5]^+$ in trimethyl phosphate with those observed in other solvents (Table 1) indicates that the ability of trimethyl phosphate to compete with the cryptands for Li^+,Na^+, Ag^+ and Tl^+ rests in between that of methanol and dimethylformamide. It competes more effectively than the aprotic oxygen donor solvent propylene carbonate ($D_N = 15.1$), but less effectively than dimethyl sulfoxide ($D_N = 29.8$) as anticipated from their D_N values. These data for two cryptands and four metal ions confirm the generality of the observation that D_N is a reasonable predictor of the variation of cryptate stability with the type of aprotic solvent. Trimethyl phosphate competes more effectively with the cryptands for Li^+, Na^+, Ag^+ and Tl^+ than does methanol despite the similarly of their D_N values (Table 1) which suggests that a $D_N < 23.5$ for methanol might be appropriate as deduced from these cryptate systems. Water competes more effectively for Li^+ and Na^+ than the other solvents listed in Table 1 (consistent with $D_N = 33.0$), but it competes less effectively than dimethyl sulfoxide for Ag^+ and Tl^+. These variations indicate that D_N values are indicative of broad trends in stability variations and that specific effects arising from variations in the nature of metal to solvent bonding or steric effects may superimpose on the broad trend.

Cryptate kinetics

Metal ion exchange rates in $[Li.C21C_5]^+$ and $[Na.C211]^+$ were obtained from complete lineshape analyses [27] of the coalescence of the resonances of the alkali metal nucleus in the free and cryptand environment, as exemplified for $[Na.C211]^+$ in Fig. 2. The derived mean life times of the alkali metal ion in the cryptates, τ_c, and the compositions of the solutions are given in Table 2. (For a given solution $\tau_c/X_c = \tau_s/X_s$, where τ_s is the mean lifetime of the alkali metal ion in the fully solvated state, and X_c and X_s are the corresponding mole fractions). The magnitudes and temperature variations of τ_c for each of the $[Li.C21C_5]^+$ solutions studied are very similar, and a similar situation applies for $[Na.C211]^+$ (Fig. 3 and Table 2). This indicates that τ_c ($= 1/k_d$, where k_d is the decomplexation rate constant) is independent of the concentration of the solvated alkali metal ion. This is consistent with the non-participation of the solvated alkali metal ion in the rate determining step of the predominant pathway for exchange on $[Li.C21C_5]^+$ and $[Na.C211]^+$, and the operation of a monomolecular mechanism for the decomplexation of the alkali metal ions from the cryptates as shown in eqn. (1) for $[Na.C211]^+$ where k_c is the complexation rate constant. The kinetic parameters for the decomplexation of $[Li.C21C_5]^+$ and $[Na.C211]^+$ (Table 2) are derived from the temperature variation of τ_c through eqn. (2) in which all symbols have their usual meaning.

$$Na^+ + C211 \underset{k_d}{\overset{k_c}{\rightleftharpoons}} [Na.C211]^+ \qquad (1)$$

$$k_d = 1/\tau_c = (k_BT/h)\exp(-\Delta H_d^{\neq}/RT + \Delta S_d^{\neq}/R) \qquad (2)$$

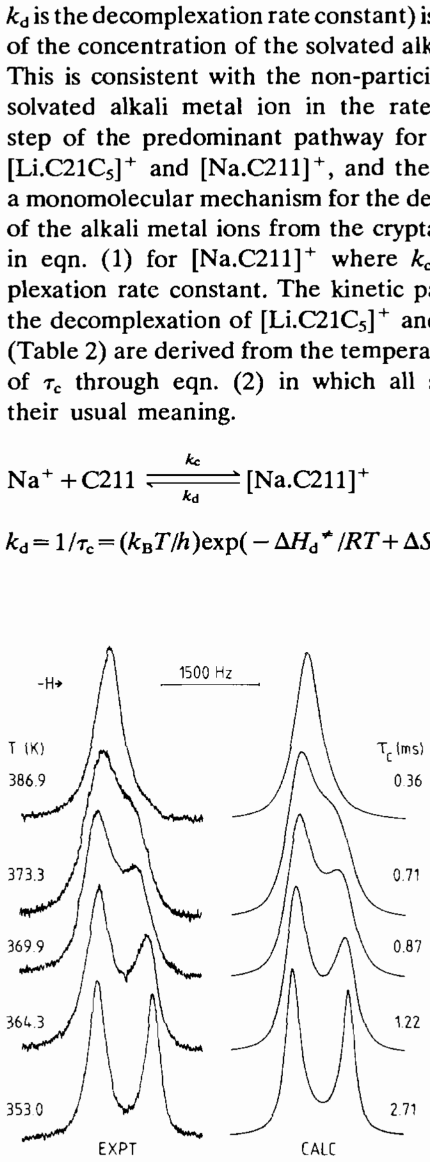

Fig. 2. Typical exchange modified 79.39 MHz ^{23}Na NMR spectra of a trimethyl phosphate solution of $NaClO_4$ (0.1002 mol dm^{-3}) and C211 (0.0571 mol dm^{-3}). Experimental temperatures and spectra appear to the left of the Fig., and the best fit calculated lineshapes and corresponding τ_c values appear to the right. The resonance of $[Na.C211]^+$ appears downfield from that of solvated Na^+.

TABLE 2. Solution compositions and kinetic parameters[a] for the decomplexation of $[Li.C21C_5]^+$ and $[Na.C211]^+$ in trimethyl phosphate

Solution	$[Li^+_{solvated}]$ (mol dm^{-3})	$[Li.C21C_5]^+$ (mol dm^{-3})	k_d (298.2 K) (s^{-1})	k_d (325.0 K)[b] (s^{-1})	$\Delta H_d^{\neq}$ (kJ mol^{-1})	$\Delta S_d^{\neq}$ (J K^{-1} mol^{-1})
i	0.0079	0.0134	22.6±0.6	193±2	61.7±1.0	−12.1±3.4
ii	0.0102	0.0111	25.9±0.9	210±4	61.1±1.3	−13.1±4.2
iii	0.0139	0.0075	23.0±0.4	180±2	59.4±0.6	−19.8±2.0
(i–iii)			23.3±0.4	195±3	61.2±1.1	−13.6±3.6
	$[Na^+_{solvated}]$ (mol dm^{-3})	$[Na.C211]^+$ (mol dm^{-3})	k_d (298.2 K) (s^{-1})	k_d (373.0 K)[b] (s^{-1})	$\Delta H_d^{\neq}$ (kJ mol^{-1})	$\Delta S_d^{\neq}$ (J K^{-1} mol^{-1})
i	0.0340	0.0661	6.88±0.87	1400±25	62.9±1.6	−17.9±4.9
ii	0.0431	0.0571	6.47±0.78	1340±20	63.1±1.5	−17.6±4.5
iii	0.0541	0.0461	6.69±0.54	1280±15	62.2±1.0	−20.6±3.1
iv	0.0735	0.0272	7.44±0.62	1270±15	60.7±1.1	−24.6±3.1
(i–iv)			6.92±0.50	1325±15	62.2±0.9	−20.3±2.7

[a] Errors represent one standard deviation from the least-squares fit of the experimental τ_c data to eqn. (2). [b] Temperature in midst of coalescence region where the most reliable kinetic data are obtained.

Metal ion exchange on $[Li.C211]^+$ is in the very slow extreme of the NMR timescale close to the boiling point of trimethyl phosphate. In contrast exchange on $[Na.C21C_5]^+$ is in the fast extreme of the NMR timescale at 298.2 K, and cooling causes precipitation of $[Na.C21C_5]ClO_4$ which precludes quantitative kinetic characterization. However, at 298.2 K an upper limit of $k_d \ll 4$ s^{-1} was calculated for $[Li.C211]^+$, and $k_d \approx 10^4$ s^{-1} was calculated for $[Na.C21C_5]^+$ using approximate methods [30].* At 298.2 K k_d increases in the sequence: $[Li.C211]^+ < [Na.C211]^+ < [Li.C21C_5]^+ < [Na.C21C_5]^+$ in trimethyl phosphate, which is a similar sequence to those observed in other solvents (Table 3). In broad terms the magnitude of k_d is dependent on the optimisation of fit between the metal ion and the cryptand cavity, the number and type of cryptand donor atoms, and the nature of the metal ion and the cryptand. Thus *inclusive* $[Li.C211]^+$ achieves an optimal fit between Li^+ and C211 which possesses six donor atoms, and is less labile than $[Li.C21C_5]^+$ which possesses one less donor atom and in consequence is more disposed to exist partially in the *exclusive* form [9] which is part way to the formation of the transition state. The lower surface charge density of Na^+ and the *exclusive* nature of $[Na.C211]^+$ are probably the major factors contributing to this cryptate being more labile

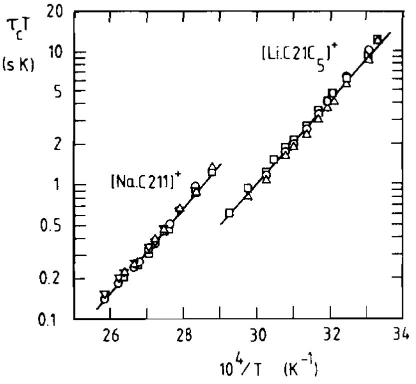

Fig. 3. The temperature variation of τ_c for Li^+ exchange on $[Li.C21C_5]^+$ in trimethyl phosphate. Data points for solutions (i)–(iii) are represented by circles, triangles, and squares, respectively. The temperature variation of τ_c for Na^+ exchange on $[Na.C211]^+$ in trimethyl phosphate. Data points for solutions (i)–(iv) are represented by circles, triangles, squares and inverted triangles, respectively. For both sets of data the solid line represents the best fit of the combined data for each set of solutions to eqn. (2).

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*In the fast exchange limit k_d may be calculated through:

$$\pi W_{1/2\ obs} \approx X_c \pi W_{1/2\ c} + X_s \pi W_{1/2\ s} + X_c^2 X_s^2 4\pi^2 (\nu_c - \nu_s)^2 (\tau_c + \tau_s)$$

where $W_{1/2}$ obs (=364 Hz) is the observed width at half amplitude of the singlet resonance arising from the environmental averaging of the resonances of $[Na.C21C_5]^+$ and $Na^+_{solvated}$, $W_{1/2\ c}$ and $W_{1/2s}$ are the width of these respective species in the absence of exchange, X_c and X_s are their mole fractions (0.45 and 0.55, respectively), and τ_c ($=1/k_d \approx 10^{-4}$ s) and τ_s are their mean lifetimes. Thus $W_{1/2\ c}$ and $W_{1/2\ s}$ = 351 and 93 Hz, respectively, determined at 298.2 K from solutions of $[Na.C21C_5]^+$ and $Na^+_{solvated}$ alone at the same total Na^+ concentration as the exchanging solutions, and the corresponding $\nu_c - \nu_s = 932$ Hz.

In the very slow exchange limit an upper limit for k_d may be obtained for $[Li.C211]^+$ through:

$$k_d \ll \pi 1.5 W_{1/2\ c} - \pi W_{1/2\ c}$$

where $1.5W_{1/2\ c}$ is the width which would be observed if the exchange rate was sufficient to increase $W_{1/2\ c}$ (=2.56 Hz) by a factor of 0.5, on which basis $k_d \ll 4$ s^{-1} at 298.2 K.

TABLE 3. Kinetic parameters for Li^+ and Na^+ exchange in several cryptates in a range of solvents

Solvent	D_N	$10^{-5}\ k_c$ (298.2 K)[a] ($dm^3\ mol^{-1}\ s^{-1}$)	k_d (298.2 K) (s^{-1})	$\Delta H_d^{\neq}$ ($kJ\ mol^{-1}$)	$\Delta S_d^{\neq}$ ($J\ K^{-1}\ mol^{-1}$)
$[Li.C211]^+$					
Methanol[b]	19.0[c] 23.5[d]	4.8	0.0044		
Trimethyl phosphate[e]	23.0[c]		$\ll 4$		
Dimethylformamide[f]	26.6[c]	1.27	0.0130	64.4	−64.8
$[Li.C21C_5]^+$					
Acetonitrile[g]	14.1[c]		slow		
Propylene carbonate[g]	15.1[c]		slow		
Acetone[g]	17.0[c]		slow		
Methanol[g]	19.0[c] 23.5[d]	0.221	21.6	36.1	−98.4
Trimethyl phosphate[e]	23.0[c]	0.058	23.3	61.2	−13.6
Dimethylformamide[g]	26.6[c]	0.073	116	38.4	−76.5
$[Na.C211]^+$					
Propylene carbonate[h]	15.1[c]	210	0.036		
Methanol[h]	19.0[c] 23.5[d]	31.0	2.5		
Trimethyl phosphate[e]	23.0[c]	16.6	6.92	62.2	−20.3
Dimethylformamide[i]	26.6[c]	19.2	12.1	83.5	55.8
$[Na.C21C_5]^+$					
Acetonitrile[j]	14.1[c]	100	84.8	57.9	−13.8
Propylene carbonate[j]	15.1[c]	25.5	19.4	70.3	15.3
Acetone[j]	17.0[c]	84	878	54.4	−6.1
Methanol[j]	19.0[c] 23.5[d]	104	1800	44.9	−31.9
Trimethyl phosphate[e]	23.0[c]		≈ 10000		
Dimethylformamide[j]	26.6[c]	214	28800	40.0	−25.3

[a] $k_c = k_d K$. [b] Ref. 10. [c] Ref. 24. The dielectric constants from the same reference are: acetonitrile 38.0, propylene carbonate 69.0, acetone 20.7, methanol 32.6, trimethyl phosphate 20.6 and dimethylformamide 36.1. [d] Refs. 25 and 26. [e] This work. [f] Ref. 17. [g] Ref. 9. [h] Ref. 15. [i] Ref. 31. [j] Ref. 8.

than $[Li.C211]^+$, and the decrease by one in the number of donor atoms in $[Na.C21C_5]^+$ results in this being the most labile of the four cryptates [8]. Solid state X-ray diffraction studies show that in [Na.C211]NCS, and $[Na.C21C_5]NCS$ the Na^+ centre is located 14 and 37 pm, respectively, above the common plane of the three oxygens of the trioxa fifteen membered cryptand ring, with a thiocyanate nitrogen in bonding distance in each case [21]. Thus, although Na^+ resides partially within the trioxa fifteen membered ring, we have chosen to apply the description *exclusive* to these structures, and anticipate that similar *exclusive* structures exist in solution with the thiocyanate interactions replaced by interactions with one or more solvent molecules.

When the exchange process is in the NMR timescale for a sufficiently wide range of solvents, as is the case for $[Na.C21C_5]^+$, a general trend emerges in which the variation of k_d with solvent is significantly greater than that of k_c so that variation in K is largely determined by the variation in k_d. This is consistent with the transition state being more similar to the solvated metal ion and the free cryptand than the cryptate. This may be understood through a simplified model in which $\Delta G_c^{\neq}$ is held invariant while $\Delta G_d^{\neq}$ varies with solvent. In the absence of solvent interaction the free energy change characterising the structural rearrangement occurring on going from the ground state to the transition state, $\Delta G_r^{\neq}$, is constant for a given cryptate, and the solvent interaction, $\Delta G_s^{\neq}$, decreases the free energy of the transition state such that $\Delta G_d^{\neq} = \Delta G_r^{\neq} - \Delta G_s^{\neq}$ (and $\Delta G_c^{\neq} - \Delta G_d^{\neq} = \Delta G^0$, the free energy of complexation). Because the free energies of the solvated metal ion and the cryptand and the cryptate are similarly changed by variation of solvent, the increase in the solvation contribution to the free energy of the transition state, $\Delta G_s^{\neq}$, with increase in solvent D_N, causes $\Delta G_d^{\neq}$ to decrease so that as k_d increases ΔG^o becomes less negative and the stability of the cryptate decreases [8]. Although this simple model rationalises the variation of $\Delta G_d^{\neq}$ and ΔG^o with change of solvent, the $\Delta H_d^{\neq}$ and $\Delta S_d^{\neq}$ contributions to $\Delta G_d^{\neq}$

vary irregularly and probably indicate the underlying intricacies of conformational and solvation changes involved in the decomplexation process. (It is seen from Table 3 that the variation of k_d characterising $[Na.C21C_5]^+$ does not exhibit an obvious correlation with the dielectric constant of the solvents, and neither does the variation of K).

Acknowledgements

The support of this project by the Australian Research Council and the award of a Commonwealth Research Scholarship to T.R. are gratefully acknowledged.

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