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Equilibrium and kinetic study of the complexation of lithium(I), sodium(I), silver(I) and thallium(I) by 4,7,13,16-tetraoxa-1,10-diazabicyclo[8.5.5]eicosane (C211) and 4,7,13-trioxa-1,10-diazabicyclo[8.5.5]eicosane ($C21C_5$) in trialkyl phosphate solvents

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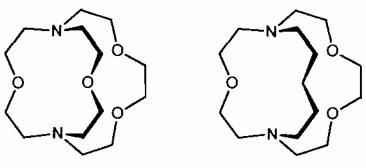
Abstract

Potentiometric titration and ^7Li and ^{23}Na NMR spectroscopy have been used to study the complexation of $M^+ = Li^+$, Na^+, Ag^+ and Tl^+ by the cryptands 4,7,13,16-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 $[M.C21C_5]^+$ in triethyl and tri-n-butyl phosphate. In triethyl phosphate the logarithm of the apparent stability constant for $[M.C211]^+$, $\log K$ (dm^3 mol^{-1}) $= 6.44 \pm 0.01$, 4.72 ± 0.01, 9.34 ± 0.10 and 2.97 ± 0.10 for $M^+ = Li^+$, Na^+, Ag^+ and Tl^+, respectively; and for $[M.C21C_5]^+$ $\log K$ (dm^3 mol^{-1}) $= 1.99 \pm 0.10$, <2, 5.68 ± 0.10 and 2.18 ± 0.10 for $M^+ = Li^+$, Na^+, Ag^+ and Tl^+, respectively. In tri-n-butyl phosphate $\log K$ (dm^3 mol^{-1}) for $[M.C211]^+ = 4.94 \pm 0.01$, 7.83 ± 0.05 and 3.36 ± 0.10 for $M^+ = Na^+$, Ag^+ and Tl^+, respectively; and for $[M.C21C_5]^+$ $\log K$ (dm^3 mol^{-1}) $= 2.36 \pm 0.10$, 1.55 ± 0.10 and 4.94 ± 0.08 for $M^+ = Li^+$, Na^+ and Ag^+, respectively. The decomplexation kinetic parameters for $[Li.C21C_5]^+$ are: k_d (298.2 K) $= 80.5 \pm 0.5$ s^{-1}, $\Delta H_d^{\ddagger} = 34.8 \pm 0.3$ kJ mol^{-1} and $\Delta S_d^{\ddagger} = -91.9 \pm 1.1$ J K^{-1} mol^{-1} in triethyl phosphate. Those for $[Na.C211]^+$ are: k_d (298.2 K) $= 8.17 \pm 0.79$ and 3.61 ± 0.49 s^{-1}, $\Delta H_d^{\ddagger} = 67.0 \pm 1.4$ and 84.7 ± 1.4 kJ mol^{-1}, and $\Delta S_d^{\ddagger} = -2.6 \pm 4.1$ and 50.5 ± 3.7 J K^{-1} mol^{-1} in triethyl phosphate and tri-n-butyl phosphate, respectively. The dominant mechanism for metal ion exchange in these three systems involves a monomolecular decomplexation of the metal ion. Metal ion exchange on $[Li.C211]^+$ and $[Na.C21C_5]^+$, respectively, is in the very slow and very fast extreme of the NMR timescale in triethyl and tri-n-butyl phosphate. These data are compared with those obtained in trimethyl phosphate and other solvents, and the influence of solvent molecular size and type on the exchange process is considered.

Introduction

The complexation of metal ions by cryptands (polyoxadiazabicycloalkanes) results in cryptates whose stabilities and labilities are dependent on the structure of the cryptands, the number and type of their donor atoms, and the nature of the metal ions and of the solvents [1–21]. In this study we consider several of these aspects through the cryptates formed 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 (C211 and $C21C_5$, respectively, as shown in Fig. 1), and are particularly interested in examining the influence of the variation of the molecular size of trialkyl phosphate solvents on cryptate stability and lability. Together with previously studied trimethyl phosphate [20], triethyl and tri-n-butyl phosphate have been selected as solvents because they are all oxygen donors, possess similar tetrahedral geometry and Gutmann donor numbers ($=D_N$, which are measures of the solvent electron donating ability, and which can have a significant influence on cryptate stability and lability [7–9]) of 23.0, 26.0 and 23.6 [22, 23], respectively, but have very different molar volumes of 115.5, 170.6 and 272.9 cm^3 mol^{-1}. (Calculated from the molar densities of trimethyl, triethyl and tri-n-butyl phosphate of 1.213, 1.068 and 0.976 g cm^{-3}, respectively.)



C211 $C21C_5$

Fig. 1. Structures of the cryptands C211 and $C21C_5$.

The cryptates formed by C211 and $C21C_5$ with Li^+, Na^+, Ag^+ and Tl^+ have been chosen to assess the

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influence of trialkyl phosphate solvent size, because their stabilities and labilities have been well characterised in other solvents [7–9, 19]. The selection of Li^+ and Na^+ is also a consequence of ^7Li and ^{23}Na possessing good NMR sensitivity which facilitates kinetic studies, and because the crystal structures of the cryptate cations $[Li.C211]^+$ and $[Li.C21C_5]^+$, and their Na^+ analogues [24–26], are available to provide a basis for discussion of their solution properties. The soft acid cations, Ag^+ and Tl^+, are chosen to provide a contrast with the hard acid Li^+ and Na^+ cations [27, 28].

Experimental

Materials

The cryptand $C21C_5$ was prepared as in the literature [26] and C211 (Merck) was distilled prior to use. Triethyl and tri-n-butyl phosphate (BDH) were distilled and dried over Linde 4 Å molecular sieves. Lithium and sodium perchlorate (Fluka) and silver nitrate (Merck) were stored over P_2O_5 under vacuum after drying under vacuum at 353–363 K for 48 h. Thallium perchlorate was prepared from Tl_2CO_3 and $HClO_4$ by metathesis in water, recrystallised twice from water and dried as described above. All solutions were prepared under dry nitrogen in a glove box.

Potentiometric titrations

Stability constants for $[Na.C211]^+$ and $[Na.C21C_5]^+$ were determined in duplicate by potentiometric titration of 25 cm^3 of 10^{-3} mol dm^{-3} $NaClO_4$ solutions with 10^{-2} mol dm^{-3} solutions of C211 or $C21C_5$. The titrations were carried out under dry nitrogen in a thermostatted (298.2 ± 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 titration and reference vessels were linked by a salt bridge containing 0.05 mol dm^{-3} Et_4NClO_4 solution. Voltage changes were determined with an Orion Research SA 720 digital analyser. The Na^+ specific electrode was replaced by a silver wire electrode in all other titrations, but the equipment used was otherwise identical. Stability constants for $[Ag.C211]^+$ and $[Ag.C21C_5]^+$ were determined through 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 used in the derivation of the stability constants of $[Li.C211]^+$ and $[Li.C21C_5]^+$ from data 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 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 lower solubility of this cryptate. All solutions were 0.05 mol dm^{-3} in Et_4NClO_4.

NMR spectroscopy

Variable temperature ^7Li and ^{23}Na NMR spectroscopic studies were carried out on solutions 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. Substantial exchange induced spectral modifications were observed over the range 40–50 K depending on the system under study, and spectra were collected at temperature intervals of *c.* 3 K within these ranges. The solution temperatures were controlled to within ± 0.3 K using a Bruker B-VT 1000 temperature controller. The Fourier transform spectra obtained at ten or more different temperatures for each solution were subjected to complete lineshape analysis [29] 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

It can be seen from Table 1 that the apparent stability constant, K, characterising $[M.C211]^+$ is greater than that of $[M.C21C_5]^+$ for the four metal ions studied in all three trialkyl phosphates, and that the stability of both cryptates is moderately greater in trimethyl phosphate than in triethyl or tri-n-butyl phosphate. The first observation may be understood from the structural variations of the cryptates. Solid state $[Li.C21C_5]^+$ and $[Li.C211]^+$ exist as inclusive cryptates [24, 25], where Li^+ resides in the cryptand cavities consistent with an

TABLE 1. Apparent stability constants for cryptates formed by some monovalent metal ions and 4,7,13,16-tetraoxa-1,10-diazabicyclo[8.5.5]eicosane (C211) and 4,7,13-trioxa-1,10-diazabicyclo[8.5.5]eicosane ($C21C_5$) in trialkylphosphates and other solvents at 298.2 K

Solvent	D_N	V_s^{a} (cm^3 mol^{-1})	log K (dm^3 mol^{-1})			
			$[Li.C211]^+$	$[Na.C211]^+$	$[Ag.C211]^+$	$[Tl.C211]^+$
Acetonitrile	14.1^{b}	52.2	$>10^{c}$	9.8^{d} 8.74^{f}	7.70^{d} 7.74^{f}	7.02^{e}
Propylene carbonate	15.1^{b}	85.9	12.44^{c}	8.76^{c}	14.44^{c}	6.58^{e}
Methanol	19.0^{b} 23.5^{g}	40.5	8.04^{c}	6.7^{d} 6.64^{f}	10.60^{c} 10.46^{f}	5.65^{e}
Trimethyl phosphate	23.0^{b}	115.5	6.98^{i}	5.38^{i}	9.82^{i}	3.95^{i}
Triethyl phosphate	26.0^{h}	170.6	6.44 ± 0.01^{j}	4.72 ± 0.01^{j}	9.34 ± 0.10^{j}	2.97 ± 0.10^{j}
Tri-n-butyl phosphate	23.7^{b}	272.9	$-^{k}$	4.94 ± 0.01^{j}	7.83 ± 0.05^{j}	3.36 ± 0.10^{j}
Dimethyl-formamide	26.6^{b}	77.4	6.99^{c}	5.23^{c}	8.60^{c}	3.15^{e}
Dimethyl sulfoxide	29.8^{b}	71.0	5.84^{c}	4.63^{c}	6.17^{c}	1.44^{c}
Water	18.0^{b} 33.0^{g}	18.1	5.5^{c}	2.8^{d} 3.2^{l}	8.5^{c}	3.19^{e}
			$[Li.C21C_5]^+$	$[Na.C21C_5]^+$	$[Ag.C21C_5]^+$	$[Tl.C21C_5]^+$
Acetonitrile	14.1^{b}	52.2	4.15^{m}	5.08^{n}	4.29^{m}	
Methanol	19.0^{b} 23.5^{g}	40.5	3.00^{m}	3.76^{n}	7.69^{m}	
Trimethyl phosphate	23.0^{b}	115.5	2.40^{i}	1.90^{i}	6.04^{i}	2.42^{i}
Triethyl phosphate[d]	26.0^{h}	170.6	1.99 ± 0.10^{j}	$<2^{j}$	5.68 ± 0.10^{j}	2.18 ± 0.10^{j}
Tri-n-butyl phosphate	23.7^{b}	272.9	2.36 ± 0.10^{j}	1.55 ± 0.10^{j}	4.94 ± 0.08^{j}	
Dimethyl-formamide	26.6^{b}	77.4	1.80^{m}	2.87^{n}	5.23^{m}	

[a] Molar volumes calculated from the densities of acetonitrile, propylene carbonate, methanol, trimethyl, triethyl and tri-n-butyl phosphate, dimethylformamide, dimethyl sulfoxide and water = 0.786, 1.189, 0.791, 1.213, 1.068, 0.976, 0.944, 1.101 and 0.997 g cm^{-3}, respectively. [b] Ref. 23. [c] Ref. 6 and refs. therein. [d] Ref. 11. [e] Ref. 14 and refs. therein. [f] Ref. 12 and refs. therein. [g] Refs. 30 and 31. [h] Ref. 22. [i] Ref. 20. [j] This work. [k] $[Li.C211]ClO_4$ was insufficiently soluble for study. [l] Ref. 10. [m] Ref. 9. [n] Ref. 7.

optimal fit of Li^+ ($r = 76$ pm [32]) 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 $[Li.C21C_5]^+$ appears to exist in a dynamic equilibrium between the inclusive and exclusive cryptates. 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]. In the solid state, exclusive structures are observed for $[Na.C21C_5]^+$ and $[Na.C211]^+$ [26] consistent with the larger size of Na^+ ($r = 102$ pm) excluding it from entry into the cavities of either cryptand. Thus, the greater K observed in trialkyl phosphate and other solvents for $[Li.C211]^+$, by comparison with that characterising $[Na.C211]^+$, may be explained in terms of the optimal fit of Li^+ into the C211 cavity resulting in increased stability (Table 1). The smaller magnitude of K for $[M.C21C_5]^+$ by comparison with that for $[M.C211]^+$ is 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 the trialkyl phosphate solvents, but is reversed in the other solvents. This may reflect the varying proportions of $[Li.C21C_5]^+$ existing in the inclusive and exclusive forms and its consequent variation in overall stability relative to $[Na.C21C_5]^+$.

In the trialkyl phosphate and other oxygen donor solvents $[Ag.C211]^+$ and $[Ag.C21C_5]^+$ are substantially more stable than their Li^+ and Na^+ analogues (Table 1) which is attributable to the tendency for the soft acid Ag^+ to bond with nitrogen donor atoms preferentially [27, 28]. 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. (Ag^+ also shows a tendency to form two strong bonds in linear array [33] which may be approximately accommodated through bonding with the two cryptand nitrogens.) In nitrogen donor acetonitrile, however, the same argument explains the reversal in stability whereby the Ag^+ cryptates become less stable than the Li^+ and Na^+ cryptates.

In the solvents listed in Table 1, $[Tl.C211]^+$ is less stable than its Li^+, Na^+ and Ag^+ analogues, except in water where its stability is comparable to that of $[Na.C211]^+$. These observations are consistent with Tl^+ interacting less strongly with C211 nitrogen donor atoms than does Ag^+. They are also consistent with the relatively large size of Tl^+ ($r = 150$ pm) decreasing 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 exclusive $[Na.C211]^+$ (for Na^+ $r = 102$ pm) in the solid state [21], which indicates that $[Ag.C211]^+$ may also exist in the exclusive form ($r = 115$ pm for Ag^+).) The lowest K value for $[Tl.C211]^+$ in Table 1 is observed in dimethyl sulfoxide which may reflect the ambidentate nature of this solvent whereby it may bond through hard oxygen to hard acids and through soft sulfur to soft acids [34]. Thus as Tl^+ is a soft acid it is possible that some dimethyl sulfoxide bonds through sulfur and competes particularly effectively for Tl^+. The low K observed for $[Ag.C211]^+$ is attributable to the same origin. In trimethyl and triethyl phosphate the stability of $[Tl.C21C_5]^+$ is similar to that of its Li^+ and Na^+ analogues which may indicate that the stabilising effect of the latter two ions being able to closely approach the six donor atoms of C211, by virtue of their smaller sizes, is lost in $C21C_5$ where all five donor atoms are disposed around one fifteen-membered cryptand ring.

The K values observed for $[M.C211]^+$ and $[M.C21C_5]^+$ in trimethyl phosphate are the highest observed in the three trialkyl phosphates indicating that trimethyl phosphate competes least effectively for the four metal ions. If increased solvent molecular size hindered competition for the metal ion it might be expected that the K values observed in tri-n-butyl phosphate (which is characterised by a very similar D_N) would be the largest whereas they are smaller than those observed in trimethyl phosphate, most markedly so in the case of Ag^+. A comparison of the K values observed for $[M.C211]^+$ and $[M.C21C_5]^+$ in the trialkyl phosphates with those observed in other solvents (Table 1) broadly indicates that the ability of the trialkyl phosphates to compete with the cryptands for Li^+, Na^+, Ag^+ and Tl^+ is greater than that of propylene carbonate and methanol, similar to that of dimethyl formamide, and less than that of dimethyl sulfoxide and water, which is largely as predicted on the basis of D_N values. (It has been suggested that $D_N = 23.5$ and 33.0, respectively, may be more appropriate for bulk methanol and water [30, 31] rather than $D_N = 19.0$ and 18.0, respectively, determined in dilute solution in dichloroethane [22].)

Cryptate kinetics

The exchange rates of Li^+ between the solvated and $[Li.C21C_5]^+$ environments, and of Na^+ between the

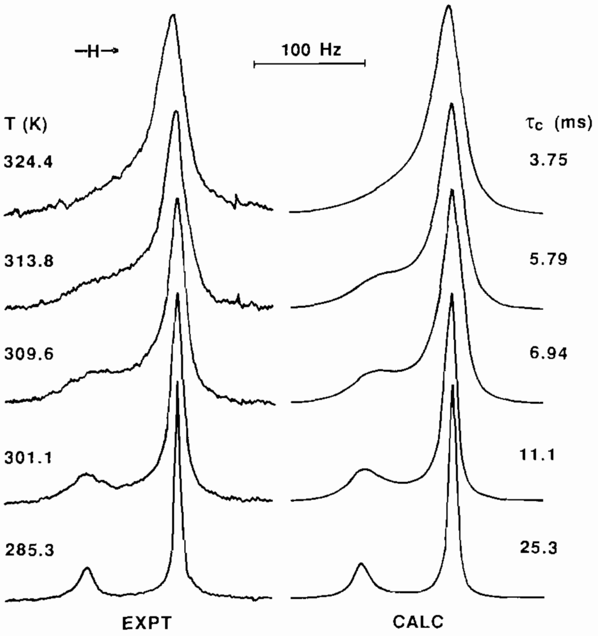

Fig. 2. Typical exchange modified 116.64 MHz ^7Li NMR spectra of a triethyl phosphate solution of $Li^+_{solvated}$ (0.0147 mol dm^{-3}) and $[Li.C21C_5]^+$ (0.0057 mol dm^{-3}). Experimental temperatures and spectra appear to the left of the Fig., and the best fit calculated lineshapes and corresponding τ_c values appear to the right.

TABLE 2. Solution compositions and kinetic parameters[a] for the decomplexation of $[\mathrm{Li.C21C_5}]^+$ and $[\mathrm{Na.C211}]^+$ in triethyl and tri-n-butyl phosphate

Solution	$[\mathrm{Li^+}_{\mathrm{solvated}}]$ (mol dm^{-3})	$[\mathrm{Li.C21C_5^+}]$ (mol dm^{-3})	k_d (298.2 K) (s^{-1})	k_d (310.0 K)[b] (s^{-1})	$\Delta H_d^‡$ (kJ mol^{-1})	$\Delta S_d^‡$ (J K^{-1} mol^{-1})
(solvent = triethyl phosphate)						
i	0.0069	0.0134	79.5 ± 0.5	142 ± 1	35.1 ± 0.4	−90.9 ± 1.3
ii	0.0106	0.0098	81.2 ± 1.1	143 ± 1	34.3 ± 0.7	−93.4 ± 2.4
iii	0.0147	0.0057	81.1 ± 1.0	144 ± 1	34.8 ± 0.6	−90.9 ± 1.3
(i-iii)			80.5 ± 0.5	143 ± 1	34.8 ± 0.3	−91.9 ± 1.1
Solution	$[\mathrm{Na^+}_{\mathrm{solvated}}]$ (mol dm^{-3})	$[\mathrm{Na.C211^+}]$ (mol dm^{-3})	k_d (298.2 K) (s^{-1})	k_d (365.0 K)[b] (s^{-1})	$\Delta H_d^‡$ (kJ mol^{-1})	$\Delta S_d^‡$ (J K^{-1} mol^{-1})
(solvent = triethyl phosphate)						
i	0.0127	0.0933	7.78 ± 1.00	1400 ± 25	67.6 ± 2.1	−1.2 ± 6.4
ii	0.0806	0.0254	8.89 ± 1.28	1490 ± 30	66.6 ± 1.9	−3.5 ± 5.8
iii	0.0530	0.0530	8.27 ± 0.99	1400 ± 40	66.1 ± 1.6	−5.7 ± 4.9
(i-iii)			8.17 ± 0.79	1410 ± 20	67.0 ± 1.4	−2.6 ± 4.1
Solution	$[\mathrm{Na^+}_{\mathrm{solvated}}]$ (mol dm^{-3})	$[\mathrm{Na.C211^+}]$ (mol md^{-3})	k_d (298.2 K) (s^{-1})	k_d (352.0 K)[b] (s^{-1})	$\Delta H_d^‡$ (kJ mol^{-1})	$\Delta S_d^‡$ (J K^{-1} mol^{-1})
(solvent = tri-n-butyl phosphate)						
i	0.0341	0.0641	2.62 ± 0.15	805 ± 6	89.7 ± 1.1	64.1 ± 2.8
ii	0.0521	0.0481	4.14 ± 0.49	885 ± 26	84.2 ± 2.0	49.3 ± 5.1
iii	0.0671	0.0331	3.97 ± 0.64	884 ± 20	84.9 ± 2.7	51.3 ± 6.8
(i-iii)			3.61 ± 0.49	859 ± 12	84.7 ± 1.4	50.5 ± 3.7

[a] Errors represent one standard deviation from the least-squares fit of the experimental τ_c data to eqn. (3). [b] Temperature in the midst of the coalescence region where the most reliable kinetic data are obtained.

solvated and $[\mathrm{Na.C211}]^+$ environments were obtained from complete lineshape analyses [29] of the coalescence of the $^7\mathrm{Li}$ and $^{23}\mathrm{Na}$ resonances, respectively, characterising the alkali metal nucleus in the solvated and cryptate environment, as exemplified for $[\mathrm{Li.C21C_5}]^+$ in Fig. 2. The derived mean lifetimes of the alkali metal ions in the cryptates, τ_c ($=1/k_d$), at two selected temperatures 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 solvated state, and X_c and X_s are the corresponding mole fractions.) An $\mathrm{Li^+}$ exchange mechanism in which the rate determining step is the monomolecular release of $\mathrm{Li^+}$ from $[\mathrm{Li.C21C_5}]^+$ may operate as shown in eqn. (1), under which circumstances τ_c ($=1/k_d$, where k_d is the decomplexation rate constant) is independent of the solvated $\mathrm{Li^+}$ concentration, and the complexation rate constant (k_c) may be derived from $K=k_c/k_d$. Alternatively, a mechanism in which $\mathrm{Li^+}$ is directly displaced from $[\mathrm{Li.C21C_5}]^+$ in the rate determining step may operate as shown in eqn. (2) such that $\tau_c=1/(k_b[\mathrm{Li^+}])$, where k_b is the bimolecular exchange rate constant. Plots of $\ln T\tau_c$ against $1/T$ for the three solutions of $[\mathrm{Li.C21C_5}]^+$ in triethyl phosphate are indistinguishable, and the derived kinetic activation parameters for the three solutions are consequently indistinguishable also (Table 2). A similar situation applies for $[\mathrm{Na.C211}]^+$ in triethyl phosphate and tri-n-butyl phosphate. (These plots are over a range of 40–50 K depending on the system under study.) This is consistent with the exchange rate being independent of the solvated metal ion concentration (Table 2), and the monomolecular mechanism shown in eqn. (1) providing the dominant exchange path in all three cases. The activation parameters for the monomolecular decomplexation of $[\mathrm{Li.C21C_5}]^+$ and $[\mathrm{Na.C211}]^+$ (Table 2) were derived from the temperature variation of k_d through eqn. (3) in which all symbols have their usual meaning. The low solubility of $[\mathrm{Li.C21C_5}]\mathrm{ClO_4}$ in tri-n-butyl phosphate precluded at $^7\mathrm{Li}$ NMR determination of the kinetic parameters characterising $[\mathrm{Li.C21C_5}]^+$.

$$\mathrm{Li^+ + C21C_5} \underset{k_d}{\overset{k_c}{\rightleftharpoons}} [\mathrm{Li.C21C_5}]^+ \qquad (1)$$

$$^*\mathrm{Li^+} + [\mathrm{Li.C21C_5}]^+ \underset{k_b}{\overset{k_b}{\rightleftharpoons}} \mathrm{Li^+} + [^*\mathrm{Li.C21C_5}]^+ \qquad (2)$$

$$k_d = 1/\tau_c = (k_b T/h)\exp(-\Delta H_d^‡/RT + \Delta S_d^‡/R) \qquad (3)$$

The $\mathrm{Na^+}$ exchange process on $[\mathrm{Na.C21C_5}]^+$ was in the fast extreme of the NMR timescale at 298.2 K, and cooling caused precipitation of $[\mathrm{Na.C21C_5}]\mathrm{ClO_4}$ which precluded quantitative kinetic characterisation. In contrast $\mathrm{Li^+}$ exchange on $[\mathrm{Li.C211}]^+$ was in the very slow extreme of the NMR timescale close to the

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

Solvent	D_N	$10^{-5}\times k_c$ (298.2 K)[a] ($dm^3\ mol^{-1}\ s^{-1}$)	k_d (298.2 K) (s^{-1})	$\Delta H_d^\ddagger$ ($kJ\ mol^{-1}$)	$\Delta S_d^\ddagger$ ($J\ K^{-1}\ mol^{-1}$)
$[Li.C211]^+$					
Methanol[b]	19.0[c] 23.5[d]	4.8	0.0044		
Trimethyl phosphate[e]	23.0[c]		≪4		
Dimethylformamide[f]	26.6[c]	1.27	0.0130	64.4	−64.8
$[Li.C21C_5]^+$					
Acetonitrile[g]	14.1[c]		slow		
Propylene[g] carbonate	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
Triethyl phosphate[h]	26.0[i]	0.079	80.5	34.8	−91.9
Dimethylformamide[g]	26.6[c]	0.073	116	38.4	−76.5
$[Na.C211]^+$					
Propylene carbonate[j]	15.1[c]	210	0.036		
Methanol[j]	19.0[c] 23.5[d]	31.0	2.5		
Trimethyl phosphate[e]	23.0[c]	16.6	6.92	62.2	−20.3
Triethyl phosphate[h]	26.0[i]	4.3	8.2	67.0	−2.6
Tri-n-butyl phosphate[h]	23.7[c]	3.1	3.6	84.7	50.5
Dimethylformamide[j]	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[k]	26.6[c]	214	28800	40.0	−25.3

[a] $k_c = k_d K$. [b] Ref. 10. [c] Ref. 23. 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. 30 and 31. [e] Ref. 20. [f] Ref. 17. [g] Ref. 9. [h] This work. [i] Ref. 21. [j] Ref. 15. [k] Ref. 8.

boiling point of triethyl phosphate. However, it has been previously shown using approximate methods [20], that at 298.2 K an upper limit of $k_d \ll 4\ s^{-1}$ applies for $[Li.C211]^+$, and $k_d \approx 10^4\ s^{-1}$ applies for $[Na.C21C_5]^+$ in trimethyl phosphate, and similar estimates are made for these cryptates in the trialkyl phosphate solvents used in this study.

At 298.2 K, k_d increases in the sequence: $[Li.C211]^+ < [Na.C211]^+ < [Li.C21C_5]^+ < [Na.C21C_5]^+$ in the trialkyl phosphates, which is a similar sequence to those observed in other solvents (Table 3). This variation reflects the influence of 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 on the decomplexation process. Thus the optimal fit between Li^+ and C211, which possesses six donor atoms, is reflected in inclusive $[Li.C211]^+$ being 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 decomplexation transition state. The exclusive nature of $[Na.C211]^+$ and the lower surface charge density of Na^+ are probably the major factors contributing to this cryptate being more labile 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]. It has been shown from solid state X-ray diffraction studies that in the exclusive cryptates [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 [26]. It is anticipated that similar exclusive structures exist in solution with the thiocyanate interactions replaced by interactions with one or more solvent molecules.

The magnitudes of k_d and k_c characterising $[Li.C21C_5]^+$ and $[Na.C211]^+$ exhibit a maximum of five-fold variation with change in trialkyl phosphate solvent. This indicates that the 2.36-fold molar volume variation exhibited by the trialkyl phosphates has only a small influence on the rate determining steps of the decomplexation and complexation processes. The monomolecular decomplexation process involves sequential conformational and solvation changes, and previous studies have indicated that, because there is often an inverse relationship between the magnitudes of k_d and K as the solvent is varied (but little variation of the magnitude of k_c), the transition state for the rate determining decomplexation process for a variety of cryptates more closely resembles the free cryptand and solvated metal ion than the ground state cryptate [8, 15]. This infers that the metal ion is partially resolvated in the cryptate transition state and that the magnitude of k_d will tend to increase with the electron donating power (D_N) of the solvent, which is broadly observed to be the case for several cryptates including $[Li.C21C_5]^+$, $[Na.C211]^+$ and $[Na.C21C_5]^+$ as seen from Table 3. (It is also seen from Table 3 that there is no obvious correlation between the variation of k_d and the solvent dielectric constant.) As the k_d data derived in the three trialkyl phosphate solvents fit into this broad trend, it appears that the molecular size of these solvents has no substantial kinetic effect. The irregular variation of $\Delta H_d^\ddagger$ and $\Delta S_d^\ddagger$ between systems probably indicates the underlying contributions of the conformational and solvational changes accompanying the decomplexation process.

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