Inorg. Chem. **1992,** *31,* 5067-5071

Complexation of Monovalent Metal Ions by 4,7,13,16-Tetraoxa-1,10-diazabicyclo[8.8.8]hexacosane in a Range of Solvents. A Potentiometric Titration and Nuclear Magnetic Resonance Study

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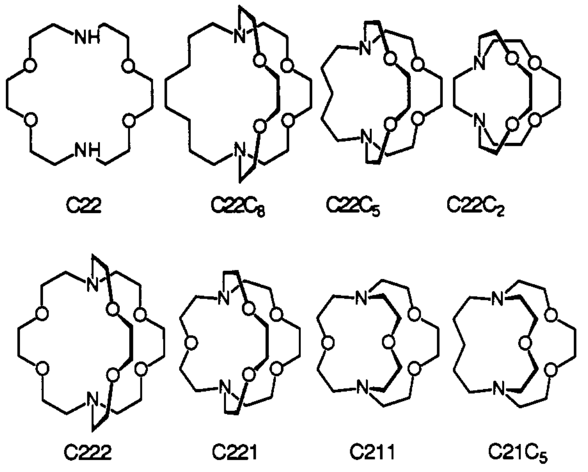
Received May 4, 1992

Complexation of Li^+, Na^+, K^+, Rb^+, Cs^+, Ag^+, and Tl^+ by 4,7,13,16-tetraoxa-1,10-diazabicyclo[8.8.8]hexacosane ($C22C_8$) to form the cryptate $[M.C22C_8]^+$ has been studied in five solvents by potentiometric titration and ^7Li and ^{23}Na NMR spectroscopy. A considerable variation in the stability of $[M.C22C_8]^+$ occurs as M^+ is varied in the sequence Li^+ (3.7, 1.9), Na^+ (4.86, 2.3), K^+ (5.09, 2.6), Rb^+ (3.85, 2.2), Cs^+ (3.13, 2.0), Ag^+ (6.23, 7.7), and Tl^+ (6.19, 3.1), where the figures in brackets are log (K/dm^3 mol^{-1}) and K is the apparent stability constant of $[M.C22C_8]^+$ in acetonitrile and dimethylformamide, respectively, at 298.2 K. The exchange of Na^+ on $[Na.C22C_8]^+$, determined by ^{23}Na NMR spectroscopy, is characterized by $k_d(298.2\ K) = 443 \pm 5$, 1253 ± 7, and $10\,800 \pm 300$ s^{-1}, $\Delta H_d^* = 38.2 \pm 0.6$, 37.1 ± 0.3, and 46.8 ± 0.6 kJ mol^{-1}, and $\Delta S_d^* = -66 \pm 2$, -61 ± 1, and -11 ± 2 J K^{-1} mol^{-1}, respectively, in acetonitrile, pyridine, and methanol. In dimethylformamide the $[Na.C22C_8]^+$ exchange rate is in the very fast regime of the ^{23}Na NMR time scale, and in acetonitrile, methanol, dimethylformamide, and pyridine the $[Li.C22C_8]^+$ exchange rate is in the very fast regime of the ^7Li NMR time scale. These data are discussed in terms of the effects of cryptand structure and of metal ion and solvent characteristics on cryptate stability and lability.

Introduction

Chart I. Diazacoronand and Cryptand Structures



The cryptand 4,7,13,16-tetraoxa-1,10-diazabicyclo[8.8.8]-hexacosane ($C22C_8$)[1-3] may be viewed as a modification of 4,7,13,16-tetraoxa-1,10-diazacyclooctadecane (C22)[4-10] where the two amine protons are replaced by the $-(CH_2)_8-$ (C_8) moiety linking the two amine nitrogens. Thus, $C22C_8$ belongs to a family of cryptands in which one arm contains no coordinating ether oxygens, the smallest reported example of which is $C22C_2$[11-13] and an intermediate-sized example of which is $C22C_5$[3,14,15] (Chart I). The C_2, C_5, and C_8 links place a constraint on the flexibility of the 18-membered 4,7,13,16-tetraoxa-1,10-diaza monocycle common to the three cryptands and C22, which should impact significantly on their selectivities in complexing metal ions and on the stability and lability of the complexes formed. Earlier studies have shown that the clamlike structure of $C22C_2$, in which the two $-(CH_2)_2O(CH_2)_2O(CH_2)_2-$ jaws are hinged about the $>N(CH_2)_2N<$ moiety, results in a selectivity pattern for alkali metal ion complexation in which there is a strong correlation among the stability of the cryptate, $[M.C22C_2]^+$, the jaw angle of $C22C_2$, and the minimizing of strain in the cryptate structure.[12,13] This mode of metal ion selectivity differs from that of cryptands such as C211, C221, and C222 (Chart I), where the selectivity is predominantly determined by the fit of the metal ion into the approximately spherical cryptand cavity whose size is largely predetermined by the bicyclic nature of the cryptand.[3,4,16-27]

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A selectivity pattern for alkali metal ions similar to that of C221 is exhibited by $C22C_5$, but the stability of $[M.C22C_5]^+$ is lower than that of $[M.C221]^+$, coincident with the presence of an additional ether oxygen in the latter cryptate.[15] Thus, in addition to making comparisons with the metal ion coordination characteristics of C22, $C22C_2$, and $C22C_5$, it is of considerable interest to compare the characteristics of $C22C_8$ with those of C222, which possesses a similar cavity size (r = 1.4 Å)[16] and two additional ether oxygens. Hence, the stabilities of $[M.C22C_8]^+$, where $M^+ = Li^+, Na^+, K^+, Rb^+, Cs^+, Ag^+$, and Tl^+, have been determined by potentiometric titration in five solvents to determine the selectivity pattern of $C22C_8$. The rates of Li^+ and Na^+ exchange in $[Li.C22C_8]^+$ and $[Na.C22C_8]^+$ have also been studied by ^{7}Li and ^{23}Na NMR spectroscopy to determine the relationship between lability and stability for these cryptates.

Experimental Section

The cryptand $C22C_8$ was prepared by a method similar to that in the literature.[3] Rubidium and cesium perchlorates were precipitated from solutions of rubidium and cesium chloride, respectively, by the addition of concentrated perchloric acid and were recrystallized from water until chloride was absent. Thallium perchlorate was prepared by reacting thallium carbonate with perchloric acid and was recrystallized from water. Potassium perchlorate (BDH) was recrystallized from water. Sodium perchlorate (Fluka) and silver perchlorate (Aldrich) were used as received after drying. All of the metal perchlorates were vacuum-dried at 353–363 K for 48 h and were then stored over P_2O_5 under vacuum.

Deionized water was ultrapurified with a MilliQ reagent system to produce water with a resistance of >15 MΩ cm. Acetonitrile, methanol, dimethylformamide, and pyridine were purified and dried by literature methods[28] and were stored under nitrogen over Linde 3-Å molecular sieves in the cases of methanol and acetonitrile and over Linde 4-Å molecular sieves for the other solvents. The water content of these solvents was below the Karl Fischer detection level of approximately 50 ppm. Solutions of anhydrous metal perchlorates and $C22C_8$ were prepared under dry nitrogen in a glovebox. For the ^{7}Li and ^{23}Na NMR studies, these solutions were transferred to 5-mm NMR tubes fitted with male B10 Quickfit joints, which were then closed by fitting into female B10 Quickfit joints attached to vacuum taps, under dry nitrogen in a glovebox. After these solutions were degassed on a vacuum line, the 5-mm NMR tubes were sealed under vacuum and coaxially mounted in 10-mm NMR tubes containing either D_2O, acetone-d_6, or dimethyl-d_6 sulfoxide, which provided the deuterium lock signal. In the case of the titration studies, the solutions were transferred to the titration vessels under dry nitrogen in a glovebox. The titration vessels were then stoppered, removed from the glovebox, and connected in the titration configuration under a dry nitrogen flow.

^{7}Li and ^{23}Na NMR spectra were run at 116.59 and 79.39 MHz on a Bruker CXP-300 spectrometer. In the ^{7}Li experiments, 1000–6000 transients were accumulated in a 8192 data point base over a 1000-Hz spectral width for each solution prior to Fourier transformation, and in the ^{23}Na experiments, 1000–6000 transients were accumulated in a 2048 data point base over an 8000-Hz spectral width for each solution. The solution temperature was controlled to within ±0.3 K using a Bruker B-VT 1000 temperature controller. The Fourier-transformed spectra were subjected to complete line shape analysis[29] on a VAX 11-780 computer to obtain kinetic data. The temperature-dependent ^{23}Na line widths and chemical shifts employed in the line shape analysis for acetonitrile, pyridine, and methanol solutions were obtained from a combination of extrapolation from low temperatures, where no exchange-induced modification occurred, and of the line width and chemical shift variations of separate solutions containing either Na^+ or $[Na.C22C_8]^+$ as the only sodium(I) species. The $[Li.C22C_8]^+$ system was in the fast-exchange regime of the ^{7}Li NMR time scale in acetonitrile, pyridine, and methanol, and estimates of the line widths and relative chemical shifts of solvated Li^+ and $[Li.C22C_8]^+$ were obtained from solutions containing either solvated Li^+ or $[Li.C22C_8]^+$ as the sole lithium(I) species.

Apparent stability constants (K, eq 1) for $[Ag.C22C_8]^+$ were determined by duplicated potentiometric titrations of 20 cm³ of 1.00 × 10^{-3} mol dm^{-3} $AgClO_4$ solution with 1.00 × 10^{-2} mol dm^{-3} $C22C_8$ solution.

$$K = [M.C22C_8{}^+]/([M^+][C22C_8]) \tag{1}$$

Apparent stability constants for $[M.C22C_8]^+$ ($M^+ = Li^+, Na^+, K^+, Rb^+, Cs^+, Tl^+$) were determined through duplicate competitive potentiometric titrations of 20 cm³ of a 1.00 × 10^{-3} mol dm^{-3} $AgClO_4$ solution with a solution 5.00 × 10^{-2} mol dm^{-3} in $MClO_4$ and 1.00 × 10^{-2} mol dm^{-3} in $C22C_8$ (except in acetonitrile in some cases, as is discussed below) as described in the literature.[22] Due to the low solubility of $KClO_4$, $RbClO_4$, and $CsClO_4$, the stability constants of $[K.C22C_8]^+$, $[Rb.C22C_8]^+$, and $[Cs.C22C_8]^{2+}$ in acetonitrile were determined from duplicate titrations of 20 cm³ of a 2.00 × 10^{-4} mol dm^{-3} $AgClO_4$ solution with a solution 5.00 × 10^{-3} mol dm^{-3} in $KClO_4$, $RbClO_4$, or $CsClO_4$ and 2.00 × 10^{-3} mol dm^{-3} in $C22C_8$. The titrations were carried out under dry nitrogen in a thermostated (298.2 ± 0.1 K) titration vessel connected to a thermostated reference vessel by a salt bridge using silver wire titration and reference electrodes, except in the case of the $[Na.C22C_8]^+$ system in pyridine, where a Radiometer G502 Na^+ specific titration electrode was used. For a given experiment, the titration and reference vessels and the salt bridge contained solutions made up in the same solvent, with the reference solution being 10^{-2} mol dm^{-3} in $AgClO_4$. All titration solutions and that in the salt bridge were 0.05 mol dm^{-3} in Et_4NClO_4. An Orion Research SA 720 digital analyzer was used to measure changes in potential for all titrations.

Potentiometric titrations in water were carried out using a Metrohm E665 Dosimat autoburet interfaced to a Laser XT/3-8086 PC together with an Orion SA720 potentiometer and an Orion Ross Sureflow 81-72 BN combination electrode. Titrations were carried out at 298.2 ± 0.1 K in a water-jacketed vessel which was closed apart from a vent to allow egress of nitrogen. A fine stream of nitrogen bubbles was passed through the titration solution to exclude atmospheric carbon dioxide, and the solution was stirred using a magnetic stirrer. The pH electrode was calibrated by titration of 0.100 mol dm^{-3} NEt_4OH (1.00 cm³) from the autoburet against 0.004 mol dm^{-3} $HClO_4$ (10.00 cm³) to determine E_0 and pK_w. (Under the conditions of this study, pK_w = 13.8.) The values of pK_{a1} = 11.1 ± 0.1 and pK_{a2} = 8.41 ± 0.05 for $H_2C22C_8{}^{2+}$ (eqs 2 and 3) were determined by titration of solutions (10.00 cm³) 0.004, 0.001,

$$K_{a1} = [H^+][HC22C_8{}^+]/[H_2C22C_8{}^{2+}] \tag{2}$$

$$K_{a2} = [H^+][C22C_8]/[HC22C_8{}^+] \tag{3}$$

and 0.100 mol dm^{-3} in $HClO_4$, $C22C_8$, and NEt_4ClO_4, respectively, with 0.100 mol dm^{-3} NEt_4OH. Attempts to determine apparent stability constants of $[M.C22C_8]^+$ ($M^+ = Li^+, Na^+, K^+, Rb^+, Cs^+$) were made by titrating similar solutions containing $MClO_4$. For each M^+, at least two titrations were performed in which the metal ion/cryptand concentration ratio was varied. However, while accurate pK_{a1} and pK_{a2} values were determined using the program MINIQUAD,[30] only upper estimates of log (K/dm³ mol^{-1}) < 2 were obtained for $M^+ = Li^+, Na^+, K^+, Rb^+$, and Cs^+.

Results and Discussion

Cryptate Stability. The selectivity of $C22C_8$ for K^+ is demonstrated by the variation of the stability of $[M.C22C_8]^+$ with M^+ in the sequence $Li^+ < Na^+ < K^+ > Rb^+ > Cs^+$ in acetonitrile and dimethylformamide (Tables I and II). A comparable pattern of selectivity is also exhibited by $[M.C222]^+$, which suggests that the similarity of the cavity sizes of C222 and $C22C_8$ (r = 1.4 Å),[16] which most closely match that of K^+ (r = 1.38 Å),[31] is a dominant factor in determining selectivity. The observation of a similar selectivity pattern for $[M.C22]^+$ indicates that the optimum cavity size formed by flexible C22 also coincides with the size of K^+.[8] The stability of $[M.C22C_8]^+$ is usually within an order of magnitude of that of $[M.C22]^+$ and seldom differs by greater than 2 orders of magnitude, but it is substantially lower than that of $[M.C222]^+$, which indicates that the two additional ether oxygens of C222 provide this cryptand with a greater ability to compete with solvent for occupancy of the first coordination sphere of M^+ (Table II). A similar relationship

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Table I. Apparent Stability Constants[a] for the Complexation of Monovalent Metal Ions by 4,7,13,16-Tetraoxa-1,10-diazabicyclo[8.8.8]hexacosane (C22C$_8$) at 298.2 K

		log (K/dm^3 mol^{-1})						
solvent	D_N[b]	[Li.C22C$_8$]$^+$	[Na.C22C$_8$]$^+$	[K.C22C$_8$]$^+$	[Rb.C22C$_8$]$^+$	[Cs.C22C$_8$]$^+$	[Ag.C22C$_8$]$^+$	[Tl.C22C$_8$]$^+$
acetonitrile	14.1	3.7 ± 0.1	4.86 ± 0.05	5.09 ± 0.05	3.85 ± 0.05	3.13 ± 0.05	6.23 ± 0.05	6.19 ± 0.05
methanol	19.0 (23.5)[c]	2.2 ± 0.1	3.4 ± 0.1				10.0 ± 0.1	
dimethylformamide	26.6	1.9 ± 0.1	2.3 ± 0.1	2.6 ± 0.1	2.2 ± 0.1	2.0 ± 0.1	7.7 ± 0.1	3.1 ± 0.1
pyridine	33.1		3.94 ± 0.05					
water	18.0 (33.0)[c]	<2	<2	<2	<2	<2		

[a] In 0.05 mol dm^{-3} Et$_4$NClO$_4$ supporting electrolyte. [b] Gutmann donor number from ref 31. [c] In refs 32 and 33, it has been suggested that the values of D_N = 33.0 and 23.5 are more appropriate in water and methanol solutions rather than D_N = 18.0 and 19.0, respectively, obtained for water and methanol in 1,2-dichloroethane solution, where the hydrogen-bonding structure of these solvents is disrupted.

Table II. Apparent Stability Constants for the Complexation of Monovalent Metal Ions by 4,7,13,16-Tetraoxa-1,10-diazabicyclo[8.8.8]hexacosane (C22C$_8$) and Other Cryptands and Diazacoronand at 298.2 K

		log (K/dm^3 mol^{-1})					
solvent	M$^+$ [a]	[M.C22C$_2$]$^+$	[M.C22C$_5$]$^+$	[M.C22C$_8$]$^+$ [b]	[M.C221]$^+$	[M.C222]$^+$	[M.C22]$^+$
acetonitrile	Li$^+$	7.8[c]	6.07[d]	3.7	10.33[e]	6.97[e]	4.39[f]
	Na$^+$	9.4[g]	7.55[d]	4.86	>11.3[e]	9.63[e]	4.49,[h] 4.30[i]
	K$^+$	7.2[g]		5.09	9.5[e]	11.3[e]	4.35,[h] 4.32[i]
	Rb$^+$			3.85	7.27[e]	9.50[e]	3.37[i]
	Cs$^+$	5.0[g]		3.13	5.15[e]	4.57[e]	2.25,[h] 2.48[i]
	Ag$^+$	9.4[c]	8.27[d]	6.23	11.24[e]	8.99[e]	7.94[j]
	Tl$^+$	10.4[g]		6.19	11.92[k]	12.30[k]	6.82[j]
methanol	Li$^+$	4.0[c]	2.30[d]	2.2	5.38[e]	2.6[e]	1.0[m]
	Na$^+$	6.6[g]	5.41[l]	3.4	8.65[e]	7.9[e]	2.04[n]
	K$^+$		5.8[d]		8.54[e]	10.4[e]	1.2[m]
	Rb$^+$		5.7[d]		6.74[e]	8.98[e]	
	Cs$^+$		4.8[d]		4.33[e]	4.4[e]	
	Ag$^+$	10.2[c]	11.13[d]	10.0	14.64[e]	12.29[e]	9.99[j]
	Tl$^+$	7.8[g]	6.48[d]		10.75[k]	10.28[k]	3.54[j]
dimethylformamide	Li$^+$	3.5[c]	2.21[d]	1.9	3.58[e]		~0[f]
	Na$^+$	6.1[g]	3.66[l]	2.3	7.93[e]	6.17[e]	<2[o]
	K$^+$	3.2[g]	3.85[d]	2.6	6.66[e]	7.98[e]	<2[o]
	Rb$^+$		3.82[d]	2.2	5.35[e]	6.78[e]	
	Cs$^+$	2.7[g]	2.90[d]	2.0	3.61[e]	2.16[e]	0.61[f]
	Ag$^+$	9.4[c]	9.40[d]	7.7	12.41[e]	10.07[e]	9.91[j]
	Tl$^+$	6.7[g]	5.05[d]	3.1	8.61[k]	8.06[k]	3.41,[j] 3.22[f]

[a] Reference 31. The six- and eight-coordinate ionic radii (Å), respectively, are as follows: Li$^+$, 0.76 and 0.92; Na$^+$, 1.02 and 1.12; K$^+$, 1.38 and 1.51; Rb$^+$, 1.52 and 1.61; Cs$^+$, 1.67 and 1.74; Ag$^+$, 1.15 and 1.28; Tl$^+$, 1.50 and 1.59. [b] This work. [c] Reference 12. [d] Reference 15. [e] Reference 24. [f] Reference 5. [g] Reference 13. [h] Reference 6. [i] Reference 7. [j] Reference 9. [k] Reference 25. [l] Reference 14. [m] Reference 3. [n] Reference 8. [o] Reference 10.

holds between the stabilities of [MC22C$_5$]$^+$ and [M.C221]$^+$ as discussed in the Introduction.

In methanol, dimethylformamide, and water, the stabilities of the alkali metal [M.C22C$_8$]$^+$ cryptates generally decrease as the electron-pair-donating power of the oxygen donor solvent increases, consistent with increasingly strong M$^+$ solvation causing a decrease in cryptate stability. (Electron-pair-donating power is proportional to the Gutmann donor number, D_N,[32] where the second values, 23.5 and 33.0, quoted for methanol and water in Table I are probably the most appropriate, as they refer to bulk solvent, whereas the values of 19.0 and 18.0 arise from determinations in 1,2-dichloroethane, where intermolecular hydrogen bonding in protic solvents is disrupted.[33,34]) The stability of [Na.C22C$_8$]$^+$ is higher than expected in pyridine for D_N = 33.1. This may indicate that the incorporation of the nitrogen donor atom in the ring structure causes pyridine to be more susceptible to a decrease in solvating power arising from steric hindrance in the Na$^+$ solvation shell. Similar trends in stability are observed for the other cryptates and [M.C22]$^+$ in Table II.

The influence of the oxygen donor solvents methanol and dimethylformamide on the stabilities of [Ag.C22C$_8$]$^+$, its thallium(I) analogue, and other silver(I) and thallium(I) species (Table II) is similar to that for the analogous alkali metal species. The particularly high stability of the silver(I) species may be attributed to the soft-acid[35,36] nature of silver(I) and its consequently greater ability to bond with the cryptand and diazacoronand nitrogens.[37,38] However, in acetonitrile the stabilities of the alkali metal species more closely approach those of their silver(I) analogues, as this nitrogen donor solvent competes more effectively for silver(I). (In the case of [K.C222]$^+$, where six ether oxygen donor atoms are present and an optimal fit of K$^+$ to the cryptand cavity is achieved, a stability substantially higher than that of [Ag.C222]$^+$ is exhibited). Thallium(I) is intermediate between the alkali metal ions and silver(I) in soft/hard-acid[25,39] character and as a consequence bonds less strongly with nitrogen donor atoms than does silver(I). As a result, the stabilities of the thallium(I) species approach, or exceed, those of their silver(I) analogues in acetonitrile, but the silver(I) species are substantially more stable than their thallium(I) analogues in methanol and dimethylformamide.

Cryptate Lability. Complete line shape analysis[29] of the temperature-dependent coalescence of the ^{23}Na resonances arising from solvated Na$^+$ and [Na.C22C$_8$]$^+$ (Figure 1) in acetonitrile,

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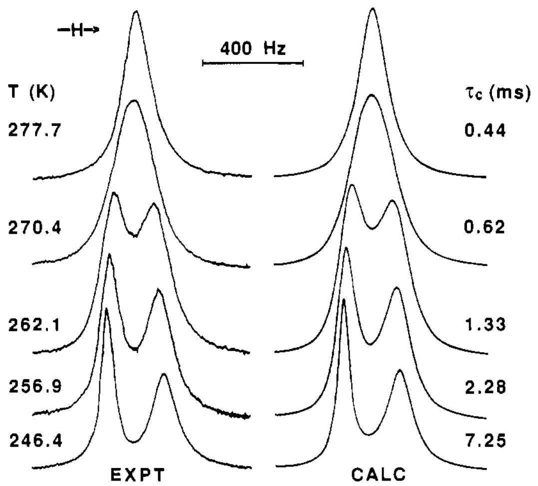

Figure 1. Typical exchange-modified 79.39-MHz ^{23}Na NMR spectra of a methanol solution of solvated Na^+ (0.0431 mol dm^{-3}) and $[Na.C22C_8]^+$ (0.0571 mol dm^{-3}). Experimental temperatures and spectra appear to the left of the figure, and the best fit calculated line shapes and corresponding τ_c values appear to the right. The resonance of $[Na.C22C_8]^+$ appears upfield from that of solvated Na^+.

pyridine, and methanol yields τ_c, the mean lifetime of Na^+ in $[Na.C22C_8]^+$, for the solutions whose compositions are given in Table III. (For a given solution $\tau_c/X_c = \tau_s/X_s$, where τ_s is the mean lifetime of Na^+ 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 solutions studied for a given solvent are very similar (Figure 2). This indicates that the mean lifetime of $[Na.C22C_8]^+$, τ_c ($=1/k_d$, where k_d is the decomplexation rate constant), is independent of the concentration of solvated Na^+ (Table III), consistent with the nonparticipation of solvated Na^+ in the rate-determining step of the predominant pathway for Na^+ exchange on $[Na.C22C_8]^+$ and the operation of a monomolecular mechanism for the decomplexation of Na^+ from $[Na.C22C_8]^+$, as shown in eq 4, where k_c ($= k_dK$) is the complexation rate constant. The kinetic parameters for the decomplexation of $[Na.C22C_8]^+$ (Table III) are derived from the temperature variation of τ_c through eq 5, where all symbols have their usual meaning.

$$Na^+ + C22C_8 \underset{k_d}{\overset{k_c}{\rightleftharpoons}} [Na.C22C_8]^+ \quad (4)$$

$$k_d = 1/\tau_c = (k_BT/h)\exp(-\Delta H_d^\ddagger/RT + \Delta S_d^\ddagger/R) \quad (5)$$

The variation in magnitude of k_d(298.2 K) in the sequence acetonitrile < pyridine < methanol is similar to the variation of k_d with the nature of the solvent observed for other sodium(I) cryptates, for which it is generally found that the magnitude of k_d(298.2 K) increases with change of solvent as D_N increases. This may be explained through a simple model where $\Delta G_c^\ddagger$ is deemed invariant, while $\Delta G_d^\ddagger$ is solvent dependent.[21] This infers that the solvation energies of the decomplexation products, Na^+ and $C22C_8$, and the $[Na.C22C_8]^+$ transition state change to a similar extent with change in solvent. Thus, in the absence of solvent interaction, the free energy change for the structural rearrangement accompanying the formation of the transition state, $\Delta G_r^\ddagger$, is constant for $[Na.C22C_8]^+$, and the solvent interaction, $\Delta G_s^\ddagger$, decreases the free energy of the transition state so that $\Delta G_d^\ddagger = \Delta G_r^\ddagger - \Delta G_s^\ddagger$ (and $\Delta G_c^\ddagger - \Delta G_d^\ddagger = \Delta G^\circ$, the complexation free energy). Therefore an increase in D_N increases $\Delta G_s^\ddagger$, and $\Delta G_d^\ddagger$ and ΔG° decrease so that $[Na.C22C_8]^+$ becomes more labile and less stable as D_N increases. On this basis, the greater D_N (=33.1) of pyridine ought to result in a larger k_d in this solvent, but for $[Na.C22C_8]^+$, as for other cryptates, this is not the case and it seems that the incorporation of the coordinating nitrogen into the aromatic ring decreases the influence of pyridine on k_d anticipated from its D_N. The variation of k_c(298.2 K) in acetonitrile, pyridine, and methanol ($10^{-7}k_c$ = 3.21, 1.09 and 2.71 dm^3 mol^{-1} s^{-1}, respectively) is considerably smaller than the variation of k_d (Table III), as is generally observed for cryptates, which suggests that the transition state is more similar to the solvated metal ion and the free cryptand than to the cryptate.[13,21,23]

In methanol and pyridine, $[Li.C22C_8]^+$ was in the fast-exchange limit of the ^{7}Li NMR time scale and no kinetic data could be derived. In acetonitrile, $[Li.C22C_8]^+$ was also in the fast-exchange limit for much of the accessible temperature range, but at 236.0 K the coalesced singlet resonance exhibited broadening which appeared to arise from a Li^+-exchange process and a lower limit for k_d of >700 s^{-1} was derived through the fast-exchange equation (6).[40] (Here $W_{1/2\text{obs}}$ = 77.4 Hz, $W_{1/2c}$ = 18.2 Hz, and $W_{1/2s}$ =

$$\pi W_{1/2\text{obs}} = X_s\pi W_{1/2s} + X_c\pi W_{1/2c} + X_s^2X_c^2(4\pi^2)(\nu_s - \nu_c)^2(\tau_s + \tau_c) \quad (6)$$

1.1 Hz, the full widths at half resonance amplitude observed for the exchanging $[Li.C22C_8]^+$ system and for $[Li.C22C_8]^+$ and Li^+ alone in separate solutions at 236.0 K; all other symbols have their usual meanings; $X_s = X_c = 0.5$ and $\nu_s - \nu_c$ = 171 Hz in the solution studied.) These observations indicate that the smaller size of Li^+, by comparison with Na^+, results in $[Li.C22C_8]^+$ being more labile than $[Na.C22C_8]^+$, probably as a consequence of the poorer fit of Li^+ to the $C22C_8$ cavity.

Because of the wide range of labilities exhibited by sodium(I) cryptates, only a limited number of systems fall within the ^{23}Na NMR kinetic time scale or that of other techniques[23] for a given solvent. Methanol is the solvent in which most data have been obtained which may be compared with those characterizing $[Na.C22C_8]^+$. These data are presented in Table IV and refer to systems for which k_d characterizes a monomolecular process. It is seen that k_d decreases in the sequence $[Na.C22C_8]^+$ > $[Na.C22C_5]^+$ > $[Na.C22C_2]^+$, consistent with the shortening of the C_n arm slowing the rate of release of Na^+ from the cryptate, probably coincident with a progressive decrease in flexibility of the cryptates. The k_d decrease in the sequence $[Na.C22C_8]^+$ > $[Na.C22C_5]^+$ > $[Na.C222]^+$ > $[Na.C221]^+$ illustrates the effect of the extra ether oxygens in the last two cryptates in slowing the release of Na^+ as a consequence of increased electrostatic interaction between C222 and C221 and Na^+; and the sequence of the last two cryptates illustrates the kinetic effect of the optimization of fit of Na^+ (r = 1.02 Å)[31] to the C221 cavity (r = 1.1 Å).[16] The inclusion of $[Na.C211]^+$ in Table IV serves to illustrate that a decrease below optimum cavity size to r = 0.8 Å increases k_d and that $C21C_5$, which has the same cavity size but one ether oxygen less, forms $[Na.C21C_5]^+$, which is of increased lability. The k_d ratio for these two cryptates is 720, while for $[Na.C22C_8]^+$ and $[Na.C222]^+$ it is 3760, coincident with these two cryptates differing by two ether oxygens and thereby representing a greater difference in electrostatic interaction between the two cryptands and Na^+ than is the case in the smaller pair of cryptates. The variation of k_d in Table IV is 4.5 × 10^5, while that in k_c is 55-fold, which illustrates the dominance of the decomplexation process in determining the relative stabilities of these cryptates.

Conclusion

The variation of the stability of $[M.C22C_8]^+$ with M^+ in the sequence $Li^+ < Na^+ < K^+ > Rb^+ > Cs^+$ in acetonitrile and dimethylformamide is consistent with the cavity size of $C22C_8$ (r = 1.4 Å)[16] best accommodating K^+ (r = 1.38 Å).[31] However,

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(40) Bovey, F. A. *Nuclear Magnetic Resonance Spectroscopy*, 2nd ed.; Academic Press: San Diego, CA, 1988.

Table III. Sodium Ion Exchange on $[Na.C22C_8]^+$ in Acetonitrile, Pyridine, and Methanol: Solution Compositions and Kinetic Parameters[a]

soln	solvent	$[Na^+(solvated)]$, mol dm^{-3}	$[Na.C22C_8{}^+]$, mol dm^{-3}	$k_d(T)$, 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}
i	acetonitrile	0.0216	0.0286	314 ± 4[b]	421 ± 5	39.1 ± 0.6	–64 ± 2
ii		0.0286	0.0216	335 ± 5[b]	446 ± 6	37.9 ± 0.7	–67 ± 2
iii		0.0372	0.0131	347 ± 7[b]	462 ± 7	37.7 ± 0.8	–67 ± 3
(i–iii)				332 ± 4[b]	443 ± 5	38.2 ± 0.6	–66 ± 2
(iv)	pyridine	0.0408	0.0613	1102 ± 9[c]	1250 ± 10	37.8 ± 1.7	–59 ± 1
(v)		0.0582	0.0439	1100 ± 10[c]	1240 ± 11	37.1 ± 0.3	–61 ± 1
(vi)		0.0766	0.0255	1144 ± 16[c]	1290 ± 16	36.0 ± 0.7	–65 ± 3
(iv–vi)				1110 ± 7[c]	1253 ± 8	37.1 ± 0.3	–61 ± 1
vii	methanol	0.0431	0.0571	1110 ± 35[d]	11600 ± 900	48.0 ± 1.7	–6 ± 6
viii		0.0581	0.0421	1090 ± 12[d]	11100 ± 280	47.5 ± 0.6	–8 ± 2
ix		0.0775	0.0226	1102 ± 6[d]	10000 ± 170	45.1 ± 0.4	–17 ± 1
(vii–ix)				1100 ± 12[d]	10800 ± 300	46.8 ± 0.6	–11 ± 2

[a] Errors represent one standard deviation from the least-squares fit of the experimental τ_c data to eq 2. [b] T = 293.4 K. [c] T = 295.9 K. [d] T = 267.3 K.

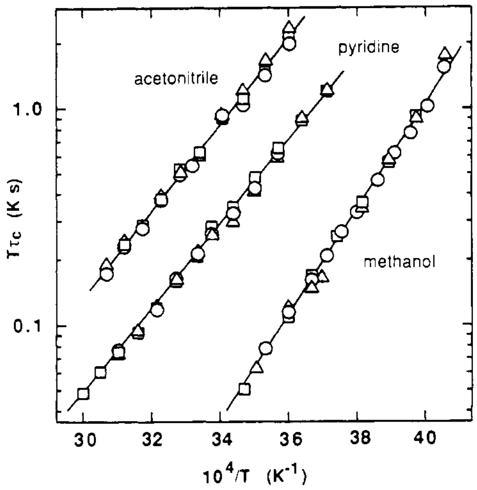

Figure 2. Temperature variation of τ_c for $[Na.C22C_8]^+$. Data points for acetonitrile solutions i–iii are represented by triangles, squares, and circles, respectively. Pyridine solutions iv–vi are represented by triangles, squares, and circles, respectively, and methanol solutions vii–ix are represented by triangles, squares, and circles, respectively. The solid lines represents the best fits of the combined data for each group of solutions to eq 2.

$[M.C22C_8]^+$ is substantially less stable than $[M.C222]^+$, which is also characterized by r = 1.4 Å and the same stability sequence. This is attributed to the presence of two more ether oxygens and a consequently greater electrostatic interaction between M^+ and C222 in $[M.C222]^+$. This is also reflected in the decomplexation of $[Na.C22C_8]^+$ (which is one of the more labile sodium(I) cryptates) being 3760 times faster than that of $[Na.C222]^+$ in methanol, which is the major reason for the much greater stability of the latter cryptate. Relative to the smaller cryptands, $C22C_2$ and $C22C_5$, $C22C_8$ tends to form less stable alkali metal and silver(I) and thallium(I) cryptates in acetonitrile, methanol, and dimethylformamide, while the stabilities of the diazacoronand complexes formed by C22 vary from being substantially less than to being 2 orders of magnitude greater than those of the cryptates formed by $C22C_8$.

Table IV. Kinetic Parameters for Na^+ Exchange on $[Na.C22C_8]^+$ and Other Cryptates in Methanol

cryptate	$10^{-5}k_c$(298.2 K), 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}
$[Na.C22C_8]^+$ [a]	271	10 800	46.7	–11
$[Na.C22C_5]^+$ [b]	520	41.0	55.1	–29.2
$[Na.C22C_2]^+$ [c]		small		
$[Na.C21C_5]^+$ [d]	104	1800	44.9	–31.9
$[Na.C222]^+$ [e]	2700	2.87		
$[Na.C221]^+$ [e]	1700	0.0235		
$[Na.C211]^+$ [e]	31.0	2.5		

[a] This work. [b] Reference 14. [c] Reference 13. [d] Reference 21. [e] Reference 23.

Acknowledgment. We thank the Australian Research Council and the University of Adelaide for supporting this research. The award of an Australian Postgraduate Research Award to A.K.W.S. is gratefully acknowledged.