spectroscopy, and Torbjorn Drakenberg (Lund) for providing data analysis programs. FT-NMR spectra (300 MHz) were obtained at The Ohio State University Chemical Instrument Center. This work was supported in part by a grant from the Elsa U. Pardee Foundation.

Registry No. ADP^{3-}, 58-64-0; 5′-AMP, 61-19-8; 5′-ATP, 56-65-5; Mg, 7439-95-4; glucose 1-phosphate, 59-56-3; glucose 6-phosphate, 56-73-5; acetyl phosphate, 590-54-5.

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Structural, Equilibrium, and Kinetic Study of the Complexation of Sodium(I) by the Cryptand 4,7,13,16-Tetraoxa-1,10-diazabicyclo[8.8.5]tricosane, $C22C_5$

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The cryptate (4,7,13,16-tetraoxa-1,10-diazabicyclo[8.8.5]tricosane)sodium(I) perchlorate, $[Na.C22C_5]ClO_4$, crystallizes in the orthorhombic space group *Pbca* with unit cell dimensions $a = 15.893$ (3) Å, $b = 15.782$ (2) Å, $c = 17.656$ (3) Å, and $V = 4428.5$ Å^3 with $Z = 8$. The structure was refined by a full-matrix least-squares procedure to final $R = 0.045$ and $R_w = 0.054$ for 1669 reflections with $I \geq 2.5\sigma(I)$. The Na^+ center is five-coordinate and lies in the same plane as the four oxygen atoms of $C22C_5$, with the fifth coordination site occupied by a perchlorate oxygen atom above this plane completing a square-pyramidal coordination geometry. An unusual feature is that the two nitrogen atoms of $C22C_5$ (which lie below the plane of the four oxygen atoms) are not within bonding distance of Na^+. This contrasts with the structure of the closely related $[Na.C221]^+$, (4,7,13,16,21-pentaoxa-1,10-diazabicyclo[8.8.5]tricosane)sodium(I), in which Na^+ is in the center of the cryptand cavity and is within bonding distance of all five oxygen atoms and both nitrogen atoms, and illustrates the major structural effect of the replacement of an oxygen donor atom of $[Na.C221]^+$ by a methylene moiety to give $[Na.C22C_5]^+$. This replacement also has a substantial effect in solution where, in acetonitrile, propylene carbonate, water, acetone, methanol, dimethylformamide, dimethyl sulfoxide, and pyridine, log (K/mol dm^{-3}) = ≥7, ≥7, 1.8, 6.09, 5.41, 3.66, 3.15, and 6.41, respectively at 298.2 K, which are substantially smaller values than those characterizing $[Na.C221]^+$. In methanol, the decomplexation kinetic parameters $k_d(298.2\ K) = 41.0 \pm 1.7\ s^{-1}$, $\Delta H_d^* = 55.1 \pm 1.1$ kJ mol^{-1}, and $\Delta S_d^* = -29.2 \pm 3.8$ kJ mol^{-1} characterizing $[Na.C22C_5]^+$ indicate that $[Na.C22C_5]^+$ is several orders of magnitude more labile than $[Na.C221]^+$. These characteristics of $[Na.C22C_5]^+$ are compared with those of related cryptates and are also discussed in terms of the reported greater efficiency of $C22C_5$ as a membrane transport carrier for Na^+ by comparison to C221.

Introduction

The cryptands, or polyoxadiazabicycloalkanes, are substrate specific receptor molecules generated through the current interest in molecular recognition chemistry. A particularly strong correlation between cation size, cryptand cavity size, cryptate structure, and thermodynamic stability is observed for the complexation of alkali-metal ions by cryptands to form cryptates.[1-9] Thus 4,7,13,16,21-pentaoxa-1,10-diazabicyclo[8.8.5]tricosane, C221 (Chart I), with a cavity radius[2] of ca. 1.10 Å, accommodates Na^+ ($r = 1.02$ Å)[10] in the center of the cavity to form *inclusive* $[Na.C221]^+$, but the larger K^+ ($r = 1.38$ Å) is too large to be accommodated, and $[K.C221]^+$ has an *exclusive* structure in which K^+ resides outside the cryptand cavity.[8] These size correlations are reflected in the variation of the stability of $[M.C221]^+$ with M^+ in the sequence $Li^+ < Na^+ > K^+$ in a range of solvents consistent with Li^+ ($r = 0.76$ Å) easily entering the C221 cavity, but being too small to establish optimal bonding distances, and *inclusive* $[Na.C221]^+$ possessing a greater stability than *exclusive* $[K.C221]^+$.[2,3,9]

One of the objectives of molecular recognition studies has been to develop substrate specific carrier molecules for membrane transport, and it is found that the replacement of a cryptand oxygen donor atom with a methylene group generally produces a more effective carrier molecule for transport of alkali-metal ions across membranes.[4] Thus 4,7,13,16-tetraoxa-1,10-diazabicyclo[8.8.5]tricosane, $C22C_5$, is a substantially more efficient carrier for Na^+ than is C221, and $C21C_5$ is a more efficient carrier for Li^+ and Na^+ than is C211. However, there have been only a few systematic studies[11-15] of the effect of the replacement of oxygen donor atoms by methylene moieties on cryptate characteristics. Accordingly a solid-state structural and solution equilibrium study of $[Na.C22C_5]^+$ is reported here, and comparisons are made with $[Na.C221]^+$, $[Na.C22]^+$ (C221 and $C22C_5$ may be viewed as C22 substituted by a $-(CH_2)_2O(CH_2)_2-$ and a $-(CH_2)_5-$ bridge between the two nitrogens, respectively), and other cryptates.

Chart I

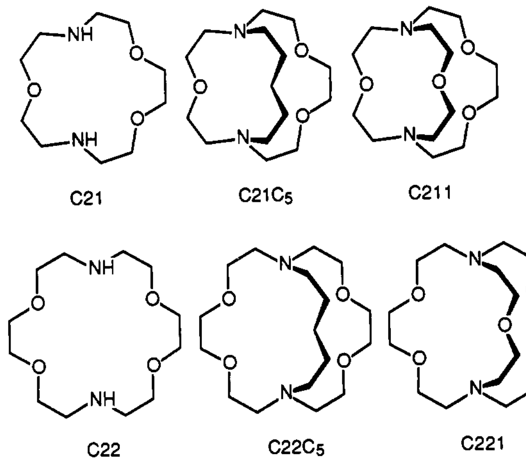

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Table I. Crystal Data for $[Na.C22C_5](ClO_4)$

formula	$C_{17}H_{34}ClN_2NaO_8$	μ, mm^{-1}	0.193
fw	452.9	θ limits, deg	1–22.5
cryst system	orthorhombic	*hkl* range	$+h,+k,+l$
space group	*Pbca* (D_{2h}^{15}, No. 61)	no. of data collcd	4574
		no. of unique data	2894
a, Å	15.893 (3)	R_{amal}[a]	0.024
b, Å	15.782 (2)	no. of unique data used with $I \geq 2.5\sigma(I)$	1669
c, Å	17.656 (3)		
V, Å^3	4428.5		
Z	8	*R*	0.045
D_{calcd}, g cm^{-3}	1.359	*g*	0.0037
F(000)	1928	R_w	0.054

[a] Where $R_{\mathrm{amal}} = (\sum\{N\sum[w(F_{\mathrm{mean}} - |F_o|^2)]\}/\sum[(N-1)\sum(w|F_o|^2)])^{1/2}$ where the inner summation is over *N* equivalent reflections averaged to give F_{mean}, the outer summation is over all unique reflections, and the weight, *w*, is taken as $[\sigma(F_o)]^{-2}$.

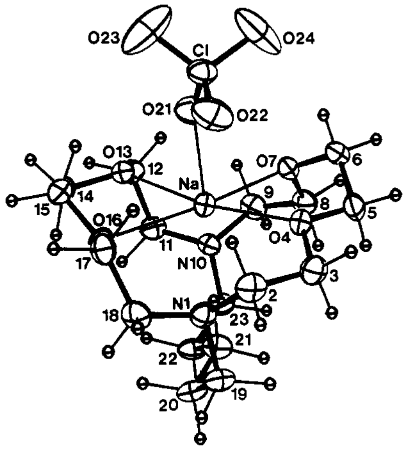

Figure 1. ORTEP plot of the structure of $[Na.C22C_5]ClO_4$ showing the atomic numbering.

Experimental Section

Materials. The cryptand $C22C_5$ has been discussed in the literature,[4] but we were unable to find details of its preparation. Accordingly, $C22C_5$ was prepared by a method similar to that used in the preparation of $C21C_5$.[14] Sodium perchlorate (Fluka) was vacuum-dried at 353–363 K for 48 h and was stored over P_2O_5 under vacuum. Crystals of $[Na.C22C_5]ClO_4$ were prepared by slow partial evaporation of an aqueous solution in which the mole ratio of $NaClO_4$ to $C22C_5$ was 1:2. Acetonitrile, propylene carbonate, acetone, methanol, dimethylformamide, dimethyl sulfoxide, and pyridine were purified and dried by literature methods,[16] and were stored under nitrogen over Linde 3-Å molecular sieves in the case of acetonitrile and methanol, and over Linde 4-Å molecular sieves in the case of the other solvents. The water content of these solvents was below the Karl-Fischer detection level of ca. 50 ppm. Deionized water was ultrapurified with a MilliQ-Reagent system to produce water with a resistance of > 15 MΩ cm.

Collection and Reduction of X-ray Data. Intensity data for a transparent crystal, 0.17 × 0.04 × 0.45 mm, were measured at room temperature, 295 K, with the use of Mo Kα (graphite monochromator) radiation ($\lambda = 0.7107$ Å) on an Enraf-Nonius CAD4F diffractometer employing the ω–2θ scan technique. No decomposition of the crystal occurred during the data collection. Corrections were applied for Lorentz and polarization effects,[17] but not for absorption. Crystal data are summarized in Table I.

Determination and Refinement of Structure. The structure was solved by direct methods and refined by a full-matrix least-squares procedure in which the function $\sum w\Delta^2$ was minimized, where *w* was the weight applied to each reflection and $\Delta = ||F_o| - |F_c||$.[18] Non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogen atoms were included in the model at their calculated positions (C–H = 1.08 Å). A weighting scheme of the form $w = [\sigma^2(F) + g|F|^2]^{-1}$ was included, and the refinement continued until the maximum shift/esd was ≤0.001. The analysis of variance showed no special features, and the maximum residual electron density peak in the final difference map was 0.28 e Å^{-3}.

Table II. Fractional Atomic Coordinates for $[Na.C22C_5](ClO_4)$

atom	*x*	*y*	*z*
Na	0.2951 (1)	0.1557 (1)	0.4033 (1)
N(1)	0.4095 (2)	0.0240 (2)	0.3364 (2)
C(2)	0.4065 (4)	0.0569 (3)	0.2590 (3)
C(3)	0.3181 (4)	0.0622 (4)	0.2283 (3)
O(4)	0.2704 (2)	0.1200 (2)	0.2734 (2)
C(5)	0.1854 (3)	0.1256 (3)	0.2497 (3)
C(6)	0.1451 (4)	0.1966 (3)	0.2926 (3)
O(7)	0.1469 (2)	0.1824 (2)	0.3726 (2)
C(8)	0.0832 (3)	0.1258 (3)	0.3992 (3)
C(9)	0.0875 (3)	0.1239 (3)	0.4840 (3)
N(10)	0.1651 (2)	0.0821 (2)	0.5097 (2)
C(11)	0.1914 (3)	0.1143 (3)	0.5841 (3)
C(12)	0.2260 (3)	0.2048 (3)	0.5799 (3)
O(13)	0.2975 (2)	0.2103 (2)	0.5312 (2)
C(14)	0.3754 (3)	0.1997 (3)	0.5693 (3)
C(15)	0.4436 (3)	0.2034 (3)	0.5120 (3)
O(16)	0.4346 (2)	0.1325 (2)	0.4628 (2)
C(17)	0.4965 (3)	0.1284 (3)	0.4045 (3)
C(18)	0.4913 (3)	0.0407 (3)	0.3719 (3)
C(19)	0.3901 (4)	−0.0674 (3)	0.3407 (3)
C(20)	0.3550 (4)	−0.0913 (3)	0.4176 (3)
C(21)	0.2731 (4)	−0.0467 (3)	0.4325 (3)
C(22)	0.2335 (3)	−0.0598 (3)	0.5093 (3)
C(23)	0.1524 (3)	−0.0105 (3)	0.5138 (3)
Cl	0.3955 (1)	0.3364 (1)	0.2978 (1)
O(21)	0.3535 (3)	0.2874 (2)	0.3540 (2)
O(22)	0.4454 (3)	0.2837 (3)	0.2510 (2)
O(23)	0.4413 (4)	0.3993 (4)	0.3339 (4)
O(24)	0.3358 (4)	0.3767 (4)	0.2526 (3)

Table III. Bond Distances (Å) for $[Na.C22C_5](ClO_4)$

Na···O(4)	2.394 (4)	Na···O(7)	2.453 (4)
Na···O(13)	2.417 (4)	Na···O(16)	2.481 (3)
Na···O(21)	2.437 (4)	N(1)–C(2)	1.463 (7)
N(1)–C(18)	1.467 (6)	N(1)–C(19)	1.476 (6)
C(2)–C(3)	1.508 (7)	C(3)–O(4)	1.428 (6)
O(4)–C(5)	1.418 (6)	C(5)–C(6)	1.496 (7)
C(6)–O(7)	1.432 (6)	O(7)–C(8)	1.429 (6)
C(8)–C(9)	1.498 (8)	C(9)–N(10)	1.470 (6)
N(10)–C(11)	1.468 (6)	N(10)–C(23)	1.478 (6)
C(11)–C(12)	1.531 (7)	C(12)–O(13)	1.426 (6)
O(13)–C(14)	1.419 (6)	C(14)–C(15)	1.484 (7)
C(15)–O(16)	1.423 (5)	O(16)–C(17)	1.426 (6)
C(17)–C(18)	1.501 (7)	C(19)–C(20)	1.515 (7)
C(20)–C(21)	1.496 (7)	C(21)–C(22)	1.507 (7)
C(22)–C(23)	1.507 (7)	Cl–O(21)	1.424 (4)
Cl–O(22)	1.417 (4)	Cl–O(23)	1.386 (5)
Cl–O(24)	1.393 (5)		

Table IV. Bond Angles (deg) for $[Na.C22C_5](ClO_4)$

O(4)···Na···O(7)	70.8 (1)	O(4)···Na···O(13)	168.9 (1)
O(4)···Na···O(16)	121.2 (1)	O(7)···Na···O(13)	99.2 (1)
O(7)···Na···O(16)	167.7 (1)	O(13)···Na···O(16)	69.1 (1)
O(4)···Na···O(21)	85.5 (1)	O(7)···Na···O(21)	98.1 (1)
O(13)···Na···O(21)	91.4 (1)	O(16)···Na···O(21)	86.4 (1)
C(2)–N(1)–C(18)	111.4 (4)	C(2)–N(1)–C(19)	112.8 (4)
C(18)–N(1)–C(19)	109.8 (4)	N(1)–C(2)–C(3)	112.7 (4)
C(2)–C(3)–O(4)	109.2 (4)	C(3)–O(4)–C(5)	112.3 (4)
O(4)–C(5)–C(6)	107.7 (4)	C(5)–C(6)–O(7)	111.9 (4)
C(6)–O(7)–C(8)	114.0 (4)	O(7)–C(8)–C(9)	107.9 (4)
C(8)–C(9)–N(10)	110.9 (4)	C(9)–N(10)–C(11)	111.1 (4)
C(9)–N(10)–C(23)	110.1 (4)	C(11)–N(10)–C(23)	109.7 (4)
N(10)–C(11)–C(12)	112.4 (4)	C(11)–C(12)–O(13)	111.8 (4)
C(12)–O(13)–C(14)	113.8 (4)	O(13)–C(14)–C(15)	108.1 (4)
C(14)–C(15)–O(16)	108.2 (4)	C(15)–O(16)–C(17)	114.1 (4)
O(16)–C(17)–C(18)	106.4 (4)	N(1)–C(18)–C(17)	112.2 (4)
N(1)–C(19)–C(20)	111.5 (4)	C(19)–C(20)–C(21)	111.3 (5)
C(20)–C(21)–C(22)	117.6 (5)	C(21)–C(22)–C(23)	109.9 (4)
N(10)–C(23)–C(22)	113.0 (4)	O(21)–Cl–O(22)	110.5 (2)
O(21)–Cl–O(23)	108.3 (3)	O(21)–Cl–O(24)	109.2 (3)
O(22)–Cl–O(23)	113.3 (3)	O(22)–Cl–O(24)	108.4 (3)
O(23)–Cl–O(24)	107.1 (4)		

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Table V. Stability Constants for (4,7,13,16-Tetraoxa-1,10-diazabicyclo[8.8.5]tricosane)sodium(I), $[Na.C22C_5]^+$, and other Sodium(I) Cryptates and Diaza Crown Ether Complexes in a Range of Solvents

		log (K/dm^3 mol^{-1}) (298.2 K)^b					
solvent	D_N^{a}	$[Na.C221]^+$	$[Na.C22C_5]^+$	$[Na.C22]^+$	$[Na.C211]^+$	$[Na.C21C_5]^+$	$[Na.C21]^+$
acetonitrile	14.1	12.4^c 10.97^e	≥7^d	3.92^e 4.49^h 4.45^g	9.8^c 8.74^e	5.08^f	
propylene carbonate	15.1	12.09^i 11.86^j	≥7^d	4.31^j 4.62^h	8.76^i 8.90^j	5.12^f	4.83^j
water	18.0 (33.0)^l	5.40^k 5.4^c	1.8 ± 0.1^d		3.2^k 2.8^c		
acetone	17.0		6.09 ± 0.14^d				
methanol	19.0 (23.5)^l	9.3^c 9.65^m 9.71^o	5.41 ± 0.06^d		6.7^c 6.64^n 6.1^p	3.76^f	
dimethylformamide	26.6	7.93^q 8.03^q	3.66 ± 0.06^d		5.23^q 5.10^r	2.87^f	2.10^r
dimethyl sulfoxide	29.8	6.98^q 6.9^c 7.24^f	3.15 ± 0.05^d		4.63^r 4.3^c		
pyridine	33.1		6.41 ± 0.02^d			3.72^f	

[a] Reference 32. [b] When supporting electrolyte is present, its type and concentration is stated after each reference. When supporting electrolyte is either absent or unspecified, only the reference is given. [c] Reference 23 (0.10 mol dm^{-3} Bu_4NClO_4). [d] This study (0.05 mol dm^{-3} Et_4NClO_4). [e] Reference 24 (I adjusted with Et_4NClO_4). [f] Reference 11 (0.05 mol dm^{-3} Et_4NClO_4). [g] Reference 25 (0.1 mol dm^{-3} Et_4NClO_4). [h] Reference 26. [i] Reference 27. [j] Reference 28 (0.05 mol dm^{-3} Et_4NClO_4). [k] Reference 29. [l] References 33 and 34. [m] Reference 1. [n] Reference 30 (0.05 mol dm^{-3} Et_4NClO_4). [o] Reference 31. [p] Reference 2 (0.01 mol dm^{-3} Et_4NBr). [q] Reference 9 (0.1 mol dm^{-3} Et_4NClO_4). [r] Reference 13.

Table VI. Sodium Ion Exchange on $[Na.C22C_5]^+$ in Methanol, Solution Compositions, and Kinetic Parameters^a

soln	$[Na^+_{solvated}]$, mol dm^{-3}	$[Na.C22C_5^+]$, mol dm^{-3}	k_d(325.0 K),^{b} 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	0.0341	0.0159	271 ± 9	42.3 ± 5.0	53.2 ± 3.1	−28.5 ± 4.7
ii	0.0257	0.0243	286 ± 3	40.2 ± 1.7	56.2 ± 1.2	−19.3 ± 4.2
iii	0.0095	0.0405	289 ± 3	37.9 ± 1.1	58.4 ± 0.7	−4.7 ± 2.3
i–iii			281 ± 3	41.0 ± 1.7	55.1 ± 1.1	−29.2 ± 3.8

[a] Errors represent 1 standard deviation from the least-squares fit of the experimental τ_c data to eq 2. [b] Temperature in midst of coalescence region where most reliable kinetic data are obtained.

Refinement details are listed in Table I.

Fractional atomic coordinates are given in Table II, bond distances and angles are given in Tables III and IV, respectively, and the numbering scheme used is shown in Figure 1, which was drawn showing 25% probability ellipsoids by using the ORTEP[19] program. The scattering factors used for Na^+ (corrected for f' and f'') were from ref 20, while those for the remaining atoms were those incorporated in SHELX76.[18]

Solution Studies. All solutions of $NaClO_4$ and $C22C_5$ were prepared under dry nitrogen in a glovebox. Stability constants for $[Na.C22C_5]^+$ were determined by duplicated potentiometric titrations of 25 cm^3 of 10^{-3} mol dm^{-3} $NaClO_4$ solutions with 10^{-2} mol dm^{-3} $C22C_5$ solutions. Both sets of solutions were 0.05 mol dm^{-3} in Et_4NClO_4. The titrations were carried out under dry nitrogen in a thermostated (298.2 ± 0.01 K) titration vessel by using an Radiometer G502 Na^+-specific electrode and an Orion Research SA 720 digital analyzer.

For variable-temperature ^{23}Na NMR spectroscopic studies, solutions were sealed under vacuum in 7-mm NMR tubes and coaxially mounted in 10-mm NMR tubes containing either D_2O, acetone-d_6 or dimethyl-d_6 sulfoxide, which provided the lock signal. ^{23}Na NMR spectra were run on a Bruker CXP-300 spectrometer operating at 79.39 MHz. For each solution an average of 6000 transients was accumulated in a 2048 point data base. Sample temperature was controlled by a Bruker B-VT1000 variable-temperature unit to within ±0.3 K. To derive kinetic data from the methanol solutions, the Fourier-transformed spectra were subjected to complete line-shape analysis[21] on a VAX 11780 computer. The ^{23}Na line widths and chemical shifts and their temperature dependences employed in the line-shape analysis were extrapolated from low temperatures, where no exchange-induced modification occurred.

Results and Discussion

Crystal Structure of $[Na.C22C_5]ClO_4$. The crystal structure determination of $[Na.C22C_5]ClO_4$ shows that the cryptate cation exists in the *exclusive* form in the solid state. The Na^+ cation forms close interactions with the four ether oxygen atoms (O(4)···Na = 2.394 (4), O(7)···Na = 2.453 (4), O(13)···Na = 2.417 (4), and O(16)···Na = 2.481 (3) Å) and lies in the best plane formed by these atoms. The equation for the plane is $0.267x + 0.912y - 0.311z = 1.281$ with the following deviations (Å): Na^+, 0.005 (2); O(4), −0.091 (3); O(7), 0.082 (3); O(13), −0.087 (3); O(16), 0.073 (3). The endocyclic nitrogens do not interact significantly with Na^+ and the Na···N(1) and N(10) distances of 3.003 (5) and 3.025 (5) Å, respectively, emphasize the *exclusive* form of the cryptate. It is seen from Figure 1 that the fifth coordination site about Na^+ is occupied by O(21), at 2.437 (4) Å, of the ClO_4^- anion. Thus to a first approximation the Na^+ may be considered to exist in a square-pyramidal environment in the solid state. The remaining interatomic distances and angles for $[Na.C22C_5]ClO_4$ are as expected and do not warrant further discussion.

The structure of *exclusive* $[Na.C22C_5]^+$ contrasts with that of *inclusive* $[Na.C221]^+$ where Na^+ occupies the center of the cryptand cavity and is within bonding distance of all five cryptand oxygens (O(4)···Na = 2.491 (2), O(7)···Na = 2.499 (2), O(13)···Na = 2.451 (2), O(16)···Na = 2.519 (2), and O(21)···Na = 2.446 (2) Å), and both cryptand nitrogen atoms (N(1)···Na = 2.703 (3) and N(10)···Na = 2.591 (2) Å).[8] This is the major structural consequence of the replacement of a donor oxygen in $[Na.C221]^+$ by a methylene moiety to produce $[Na.C22C_5]^+$. It demonstrates that, although $C22C_5$ is in the endo–endo configuration where the nitrogen lone pairs are directed toward the center of the cryptand cavity in $[Na.C22C_5]^+$, the overall effect is that the electrostatic attraction of these lone pairs is insufficient to attract Na^+ to the cryptand center to form an *inclusive* cryptate. In contrast, both $[Li.C211]^+$ and $[Li.C21C_5]^+$ (Li^+ r = 0.76 Å; cavity radius[2] of C211 and $C21C_5$ is ca. 0.80 Å) exist in the *inclusive* form in the solid state, despite the absence of an oxygen in the C_5 arm of $C21C_5$.[14] As $C21C_5$ is less flexible than the larger $C22C_5$, it is possible that the formation of *inclusive* $[Li.C21C_5]^+$ is a consequence of the fortuitiously appropriate disposition of the

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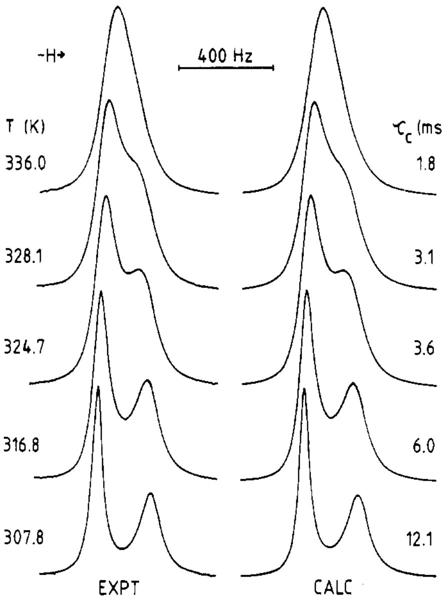

Figure 2. Typical exchange modified 79.39-MHz ^{23}Na NMR spectra of a methanol solution of $NaClO_4$ (0.0500 mol dm^{-3}) and $C22C_5$ (0.0243 mol dm^{-3}). Experimental temperatures and spectra appear to the left of the figure, and the best-fit calculated line shapes and corresponding τ_c values appear to the right. The resonance of $[Na.C22C_5]^+$ appears upfield from that of solvated Na^+.

five $C21C_5$ donor atoms, whereas this is not the case for $C22C_5$ where the C_5 ring apparently prevents the attainment of a conformation similar to that of C22 in $[K.C22]^+$, where all six donor atoms bind K^+.[22] (No $[Na.C22]^+$ structure is available for comparison.)

Solution Stability Studies. The apparent stability constants (*K*) for $[Na.C22C_5]^+$ and related species in a range of solvents appear in Table V.[1,2,9,11,13,23-31] Apart from the values determined in water and pyridine, there is a general decrease in *K* for $[Na.C22C_5]^+$ as the solvent electron-donating ability increases (as indicated by increasing Gutmann donor numbers, D_N[32]) consistent with increasingly strong Na^+ solvation causing a decrease in cryptate stability. A similar trend is also observed for the related cryptates and diaza crown ether complexes. Water does not fit this trend for its originally assigned $D_N = 18.0$, but it does fit the trend when assigned the revised value of 33.0, which is probably more appropriate for aqueous solutions rather than the value of 18.0, which characterizes water in 1,2-dichloroethane solution where the hydrogen-bonding structure of water is disrupted.[33,34] (Similarly $D_N = 23.5$ may be more appropriate in methanol solution than is the original $D_N = 19.0$.) In the case of pyridine, it is possible that the incorporation of the donor atom in the ring structure may cause sufficient steric hindrance to decrease its ability to compete with cryptands for Na^+ in pyridine solution.

In dimethylformamide the magnitude of *K* decreases in the sequence $[Na.C221]^+ > [Na.C211]^+ > [Na.C22C_5]^+ > [Na.C21C_5]^+ > [Na.C21]^+$, consistent with the optimum bonding distances achieved between Na^+ and C221 in *inclusive* $[Na.C221]^+$ resulting in the highest stability. This trend in stability is also seen in the other solvents. The cryptates $[Na.C211]^+$, $[Na.C22C_5]^+$, and $[Na.C21C_5]^+$ all exist in the *exclusive* form.[7] In the cases of $[Na.C211]^+$ and $[Na.C21C_5]^+$, both nitrogen atoms and all of the oxygen atoms of the cryptands are within bonding distance of Na^+, whereas only the oxygen atoms are within bonding distance of Na^+ in $[Na.C22C_5]^+$. Nevertheless, the coplanarity of Na^+ with the cryptand oxygens in $[Na.C22C_5]^+$ induces a greater thermodynamic stability in solution than is the case in $[Na.C21C_5]^+$ where Na^+ is 0.37 Å above the plane of the cryptand oxygens. The lower stabilities of $[Na.C22]^+$ and $[Na.C21]^+$ suggest that the more rigid structures of $[Na.C22C_5]^+$ and $[Na.C21C_5]^+$, confered by the C_5 arm, enhance stability despite these cryptates being in the *exclusive* form.

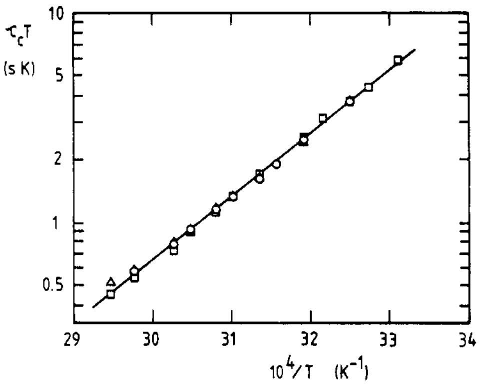

Figure 3. Temperature variation of τ_c for Na^+ exchange on $[Na.C22C_5]^+$ in methanol. Data points for solutions i–iii are reprsented by triangles, circles, and squares, respectively. The solid line represents the best fit of the combined data for the three solutions to eq 2.

Solution Kinetic Studies. In methanol, a temperature-dependent coalescence of the ^{23}Na resonances arising from solvated Na^+ and $[Na.C22C_5]^+$ (Figure 2) yields the kinetic parameters for the decomplexation of $[Na.C22C_5]^+$ (eq 1) shown in Table VI. These

$$Na^+ + C22C_5 \underset{k_d}{\overset{k_c}{\rightleftharpoons}} [Na.C22C_5]^+ \qquad (1)$$

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

parameters are derived from the temperature variation of the mean lifetime of $[Na.C22C_5]^+$, τ_c, through eq 2 in which all symbols have their usual meaning. The τ_c values ($\tau_c/X_c = \tau_s/X_s$, where τ is a lifetime, X is a mole fraction, and the subscripts c and s refer to $[Na.C22C_5]^+$ and $Na^+_{solvated}$, respectively) are derived through complete line-shape analysis[21] of the coalescing ^{23}Na resonances observed for solutions i–iii (Table VI), as exemplified by Figure 2.

It is seen from Figure 3 that the temperature variations of τ_c for each of the solutions studied for a given solvent are indistinguishable. Thus the mean lifetime of $[Na.C22C_5]^+$, τ_c ($=1/k_d$), is independent of the $[Na^+_{solvated}]$ (Table VI), consistent with the nonparticipation of $Na^+_{solvated}$ in the rate-determining step of the predominant pathway for Na^+ exchange on $[Na.C22C_5]^+$ and the operation of a monomolecular mechanism for the decomplexation of Na^+ from the cryptand. A value of $k_c(289.2\ K) = 1.05 \times 10^7$ dm^3 mol^{-1} s^{-1} calculated through the relationship $k_c = k_d K$ is within the range usually observed for cryptates.

A quantitative study of the lability of $[Na.C22C_5]^+$ in acetonitrile, acetone, and water was prevented by the solubility of $[Na.C22C_5]ClO_4$ being insufficient for reliable ^{23}Na NMR studies in these solvents. A single exchange-broadened ^{23}Na NMR signal was observed in dimethyl sulfoxide and propylene carbonate solutions containing solvated Na^+ and $[Na.C22C_5]^+$ at temperatures just above the freezing point, indicating exchange between these two sites to be in the fast exchange limit of the NMR time scale. Approximate upper limits for apparent decomplexation rate

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constants k_d ($=1/\tau_c$) ≥ 3000 s^{-1} in dimethyl sulfoxide at 300 K, and $k_d \geq 265$ s^{-1} in propylene carbonate at 280 K were calculated from the fast exchange limiting equation.[35] In dimethylformamide, a broad resonance was observed at 220 K, which partially resolved into two broad coalescing resonances ($[Na.C22C_5]^+$ upfield) in the range 240–280 K (this broadening probably arises from a combination of viscosity and exchange broadening dominating at lower and higher temperatures, respectively) and at higher temperatures coalesced to a single resonance consistent with exchange entering the fast exchange limit. While the resolution of this coalescence was insufficient for the quantitative derivation of exchange rate constants through a line-shape analysis, $k_d \approx 500$ s^{-1} (270 K) was calculated from the equation for coalescence.[35] In contrast, two well-resolved ^{23}Na resonances were observed for solvated Na^+ and $[Na.C22C_5]^+$ (485 Hz upfield at 360 K) in pyridine. At the highest temperature studied, 360 K, no significant broadening of the resonances was observed, consistent with exchange between the solvated Na^+ and $[Na.C22C_5]^+$ environments being in the very slow exchange limit from which $k_d \leq 500$ s^{-1} was calculated.[35]

For $[Na.C221]^+$, k_d(298.2 K) = 0.75, 0.25, and 0.0196 s^{-1} are reported in dimethyl sulfoxide, dimethylformamide,[36] and methanol,[37] from which it is apparent that $[Na.C22C_5]^+$ is substantially more labile in these solvents. Similarly both $[Na.C21C_5]^+$ and $[Li.C21C_5]^+$ are more labile than their C211 analogues.[12,15]

Conclusion

The replacement of an oxygen by a methylene moiety results in a structural change from *inclusive* $[Na.C221]^+$ to *exclusive* $[Na.C22C_5]^+$ in the solid state. This produces a substantial decrease and increase in the stability and lability, respectively, of $[Na.C22C_5]^+$ in solution by comparison to $[Na.C221]^+$. The decreased stability and increased lability of $[Na.C22C_5]^+$ arises from both the decrease in electrostatic attraction of $C22C_5$ for Na^+ resulting from the replacement of an oxygen donor atom by a methylene moiety, and from the change from an *inclusive* structure for $[Na.C221]^+$ to an *exclusive* structure for $[Na.C22C_5]^+$. In a membrane transport system, this should result in a greater proportion of $C22C_5$ being available for back-diffusion across a membrane, which together with the greater lability of $[Na.C22C_5]^+$, accounts for greater efficiency of $C22C_5$ as a Na^+ carrier by comparison to C221.[4] These observations are consistent with the efficiency of a given cryptand in transporting different alkali-metal ions across membranes tending to increase in the sequence in which the thermodynamic stabilities and labilities of the cryptates decrease and increase, respectively.[4]

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Supplementary Material Available: Listings of atomic coordinates and anisotropic thermal parameters (Table S(1)), hydrogen atom parameters (Table S(2)), and sample potentiometric titration data (Tables S(4) and S(5)) (5 pages); a listing of structure factors (Table S(3)) (10 pages). Ordering information is given on any current masthead page.

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$$\pi W_{1/2\,\mathrm{obs}} = X_c \pi W_{1/2\,c} + X_s \pi W_{1/2\,s} + X_c^2 X_s^2 4\pi^2 (\nu_c - \nu_s)^2 (\tau_c + \tau_s) \quad (3)$$

where $W_{1/2\,\mathrm{obs}}$ (310 and 160 Hz for the dimethyl sulfoxide and propylene carbonate solutions, respectively) is the observed width at half-amplitude of the singlet resonance arising from the environmental averaging of the resonances of $[Na.C22C_5]^+$ and Na^+_{solvated}, $W_{1/2\,c}$ and $W_{1/2\,s}$ are the widths of these respective species in the absence of exchange, X_c and X_s are their mole fractions, and τ_c ($=1/k_d$) and τ_s are their mean lifetimes. In the cases of dimethyl sulfoxide and propylene carbonate, $W_{1/2\,c}$ and $W_{1/2\,s}$ = 265 and 60 Hz and 760 and 92 Hz, respectively, determined from solutions of $[Na.C22C_5]^+$ and Na^+_{solvated} alone at the same temperatures and total Na^+ concentration as that of the exchanging solutions and with the corresponding $\nu_c - \nu_s = 530$ Hz. At the coalescence temperature an approximate k_d may be obtained through

$$1/k_d = 2^{1/2}/\pi(\nu_c - \nu_s) \quad (4)$$

when X_c and X_s are equal, and where ν_c and ν_s are the frequencies of $[Na.C22C_5]^+$ and Na^+_{solvated} in the absence of exchange. In the case of the dimethylformamide solution, $\nu_c - \nu_s = 241$ Hz was determined from solutions of $[Na.C22C_5]^+$ and Na^+_{solvated} alone at the same temperature and total Na^+ concentration as that of the exchanging solution. In the very slow exchange limit an upper limit for k_d may be obtained through

$$k_d = \pi 1.5 W_{1/2\,c} - \pi W_{1/2\,c} \quad (5)$$

where $1.5W_{1/2\,c}$ is the width that would be observed if the exchange rate was sufficient to increase $W_{1/2\,c}$ (175 Hz) by a factor of 0.5.

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Reactions of Nitroplatinum Complexes. 1. ^{15}N and ^{195}Pt NMR Spectra of Platinum(II) Nitrite Complexes[1]

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^{15}N and ^{195}Pt NMR spectra have been used to characterize the products of reaction of $Pt(^{15}NO_2)_4^{2-}$ with sulfamic acid, $Pt(^{15}NO_2)_3(H_2O)^-$ and *cis*-$Pt(^{15}NO_2)_2(H_2O)_2$, and the hydroxo complexes $Pt(^{15}NO_2)_3(OH)^{2-}$ and *cis*-$Pt(NO_2)_2(OH)_2^{2-}$ derived from them by deprotonation. At intermediate pH values, the dinitro complexes rapidly form the hydroxo-bridged compounds $[\{Pt(^{15}NO_2)_2(\mu\text{-}OH)\}_n]^{n-}$ ($n = 2, 3$). The acid dissociation constant for $Pt(^{15}NO_2)_3(H_2O)^-$ (pK_a 5.32) was determined from the variation with pH of δ_N for nitro ligands cis to water/hydroxide. ^{15}N and ^{195}Pt NMR parameters were obtained for the series $Pt(^{15}NO_2)_3Z^{m-}$. The changes in these parameters as Z was changed correlated with those in the series $Pt(^{15}NH_3)_3Z^{n+}$. δ_N and J(Pt–N) values are much more sensitive to change in the ligand Z for the nitro ligand trans to Z than for that cis to Z.

Introduction

When ammine or amine ligands bound to platinum are highly enriched in ^{15}N ($I = {}^1/_2$), ^{15}N and ^{195}Pt NMR spectra can be very useful in elucidating the solution chemistry of these complexes.[2-10] We have previously studied[11] the effect of the ligand Z on ^{15}N and ^{195}Pt NMR parameters in the series $Pt(^{15}NH_3)_3Z^{n+}$.[12]

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