Complexation of Alkali Metal Ions by the Cryptand 4,7,13,16-Tetraoxa-1,10-diazabicyclo[8.8.5]tricosane, $C22C_5$. A Structural and Equilibrium Study

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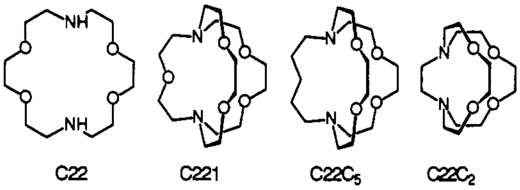
The crystal structures of the cryptates formed between 4,7,13,16-tetraoxa-1,10-diazabicyclo[8.8.5]tricosane and three monovalent cations, $[M.C22C_5]ClO_4$, have been determined. $[H_3O.C22C_5]ClO_4$, $C_{17}H_{37}ClN_2O_9$, crystallizes in the monoclinic space group $P2_1/n$ with unit cell dimensions $a = 14.166$ (2) Å, $b = 10.955$ (2) Å, $c = 15.007$ (1) Å, and $V = 2286.5$ Å^3 with $Z = 4$. The structure was refined by a full-matrix least-squares procedure to final $R = 0.077$ and $R_w = 0.086$ for 2006 reflections with $I \geq 2.5\sigma(I)$. $[K.C22C_5]ClO_4$, $C_{17}H_{34}ClKN_2O_8$, crystallizes in the triclinic space group $P\bar{1}$ with unit cell dimensions $a = 13.596$ (2) Å, $b = 15.241$ (2) Å, $c = 11.765$ (1) Å, $\alpha = 100.12$ (1)°, $\beta = 98.52$ (1)°, $\gamma = 100.66$ (1)°, and $V = 2317.1$ Å^3 with $Z = 4$. The structure was refined by a block-matrix least-squares procedure based on F to final $R = 0.045$ and $R_w = 0.051$ for 3087 reflections with $I \geq 2.5\sigma(I)$. $[Cs.C22C_5]ClO_4$, $C_{17}H_{34}ClCsN_2O_8$, crystallizes in the monoclinic space group $P2_1/n$ with unit cell dimensions $a = 15.666$ (4) Å, $b = 9.535$ (2) Å, $c = 16.335$ (4) Å, $\beta = 102.55$ (2)°, and $V = 2381.7$ Å^3 with $Z = 4$. The structure was refined by a full-matrix least-squares procedure to final $R = 0.037$ and $R_w = 0.040$ for 2206 reflections with $I \geq 2.5\sigma(I)$. In $[H_3O.C22C_5]ClO_4$, the O atom of H_3O^+ lies 0.666 (3) Å above the mean plane of the four $C22C_5$ oxygen atoms. In $[K.C22C_5]ClO_4$, K^+ lies 0.369 (1) and 0.441 (1) Å above the mean plane of the four $C22C_5$ oxygens in the two independent cryptate molecules found in the crystal. In $[Cs.C22C_5]ClO_4$, Cs^+ lies 1.2996 (3) Å above the mean plane of the four $C22C_5$ oxygens, in contrast to the case of $[Na.C22C_5]ClO_4$, where Na^+ lies 0.011 (2) Å below the mean plane of the four $C22C_5$ oxygens. The variation of the apparent stability constant for $[M.C22C_5]^+$, K (expressed as log (K/mol dm^{-3}) values), with the nature of M^+ in methanol, dimethylformamide, and water, respectively, is 2.30, 2.21, and 2.08 when $M^+ = Li^+$; 5.41, 3.66, and 2.58 when $M^+ = Na^+$; 5.8, 3.85, and 3.41 when $M^+ = K^+$; 5.7, 3.82, and 3.28 when $M^+ = Rb^+$; 4.8, 2.90, and 3.31 when $M^+ = Cs^+$; 6.48, 5.05, and 4.10 when $M^+ = Tl^+$; and 11.13, 9.40, and 9.31 when $M^+ = Ag^+$ at 298.2 K. Correlations between these variations in K and cryptate structure with the nature of M^+ are sought.

Introduction

The selective complexation of metal ions by cryptands and the stability of the cryptates formed are dependent on the relative sizes of the cryptand cavity and the metal ion, the structural flexibility and the number and type of donor atoms of the cryptand, and the solvation energy of the metal ion.[1-10] In this study we seek to clarify the interactions between these factors for systems based on the 18-membered 4,7,13,16-tetraoxa-1,10-diaza ring (Chart I) through a comparison of new structural and equilibrium data with those from the literature. Previous studies show that 4,7,13,16,21-pentaoxa-1,10-diazabicyclo[8.8.5]tricosane, C221, with a cavity radius[2] of ca. 1.10 Å, accommodates Na^+ (r = 1.02 Å)[11] in the center of the cavity to form *inclusive* $[Na.C221]^+$ but that K^+ (r = 1.38 Å) is too large to be accommodated, and as a consequence $[K.C221]^+$ has an *exclusive* structure in which K^+ resides outside the cryptand cavity on the face of the 4,7,13,16-tetraoxa-1,10-diaza ring.[5] This is 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) readily entering the C221 cavity but being too small to establish optimal bonding distances, the *inclusive* structure and optimal bonding distances of $[Na.C221]^+$ conferring a greater stability on this cryptate than that of *exclusive* $[K.C221]^+$.[2,9]

Chart I. 4,7,13,16-Tetraoxa-1,10-diazacyclooctadecane and Related Cryptands



In contrast, the monocyclic diaza crown complex (4,7,13,16-tetraoxa-1,10-diazacyclooctadecane)potassium(I), $[K.C22]^+$, has a structure in which K^+ and the four ether oxygens are coplanar and the two amine nitrogens are on opposite sides of this plane coincident with the macrocyclic hole of C22 having a radius of 1.3–1.6 Å and being sufficiently large to accommodate K^+.[12] This is an interesting structural variation, as C22 may be viewed as the monocyclic precursor of C221 and the structural differences between their metal complexes are attributable to the presence of an extra oxygen donor atom in C221 and the decreased flexibility of its 4,7,13,16-tetraoxa-1,10-diaza ring. The lower stabilities of the alkali metal species, $[M.C22]^+$,[1,13-16] in solution

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by comparison with their $[M.C221]^+$ analogues[1,2,6] may also be attributed to the same origins.

The cryptand 4,7,13,16-tetraoxa-1,10-diazabicyclo[8.8.5]-tricosane, $C22C_5$,[3,8] is similar in structure and cavity size to C221, but its donor atoms are confined to the 4,7,13,16-tetraoxa-1,10-diaza ring as in C22 and are of the same number and type. Thus, quite apart from its own intrinsic interest, the structural and equilibrium study of the alkali metal $[M.C22C_5]^+$ cryptates now reported offers an opportunity to differentiate between the origins of the structural and stability differences observed between $[M.C22]^+$ and $[M.C221]^+$ and also provides an interesting comparison with the $[M.C22C_2]^+$ cryptates, in which the 4,7,13,16-tetraoxa-1,10-diaza ring is highly constrained by the short ethylene bridge between the amine nitrogens.[9,10] The variations in shape and size of the cavities of C22, C221, $C22C_5$, and $C22C_2$ are shown qualitatively in Chart I.

Experimental Section

Materials. Although the cryptand $C22C_5$ has been discussed in the literature,[3] we were unable to find details of its preparation, and accordingly it was prepared by a method similar to that used in the preparation of $C21C_5$.[7] Methanol and dimethylformamide were purified and dried by literature methods[17] and were stored under nitrogen over Linde 3-Å molecular sieves in the case of methanol and acetonitrile and over Linde 4-Å molecular sieves in the case of dimethylformamide. 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.

Cesium and rubidium perchlorates were precipitated from solutions of cesium chloride or rubidium chloride (BDH) by the addition of concentrated perchloric acid and were recrystallized from water until chloride was absent. Thallium perchlorate was prepared by reacting thallium carbonate (BDH) with perchloric acid and was recrystallized from water. Potassium perchlorate (BDH) was recrystallized from water. Lithium and sodium perchlorates (Fluka) and silver perchlorate (Aldrich) were used as received after drying. Tetraethylammonium perchlorate was precipitated from concentrated aqueous NEt_4Br (Aldrich) solutions with perchloric acid and was recrystallized from water until bromide was absent. All of the perchlorates were vacuum-dried at 353–363 K for 48 h and then stored over P_2O_5 under vacuum.

Crystals of $[K.C22C_5]ClO_4$ and $[Cs.C22C_5]ClO_4$ were prepared by placing saturated aqueous 1:1 mole ratio solutions of $KClO_4$ or $CsClO_4$ and $C22C_5$ in a refrigerator for 48 h. Crystals of $[H_3O.C22C_5]ClO_4$ were obtained when a concentrated solution of $C22C_5$ in 1:1 volume ratio 0.05 mol dm^{-3} aqueous $HClO_4$ and acetonitrile was placed in a refrigerator for 1 week. We were unable to prepare crystals of $[Li.C22C_5]ClO_4$ and $[Rb.C22C_5]ClO_4$ suitable for X-ray diffraction studies.

Collection and Reduction of X-ray Data. Intensity data sets for transparent crystals of $[M.C22C_5](ClO_4)$ were measured at room temperature on an Enraf-Nonius CAD4F diffractometer fitted with Mo Kα radiation (graphite monochromator), $\lambda = 0.7107$ Å. The M = H_3O and Cs crystals were block-shaped and had dimensions 0.25 × 0.25 × 0.60 and 0.26 × 0.34 × 0.56 mm, respectively. The crystal chosen of the M = K complex was approximately spherical with a diameter of 0.4 mm. The ω–2θ scan technique was employed in each case, and data sets were collected up to a maximum Bragg angle of 22.5°. No significant decomposition of any crystal occurred during its respective data collection. Lorentz and polarization corrections were applied,[18] and for the M = Cs data set an analytical absorption correction was also applied (SHELX76)[19] such that the maximum and minimum transmission factors were 0.668 and 0.579, respectively. The space groups were determined unambiguously on the basis of the metric crystal data and, in the case of the M = H_3O and Cs species, by the systematic absences associated with the $0k0$ and $h0l$ classes of reflections. Crystal data are summarized in Table I.

Table I. Crystal Data for $[M.C22C_5]ClO_4$

M^+	H_3O^+	K^+	Cs^+
formula	$C_{17}H_{37}ClN_2O_9$	$C_{17}H_{34}ClKN_2O_8$	$C_{17}H_{37}CsClN_2O_8$
fw	448.9	469.0	562.8
cryst syst	monoclinic	triclinic	monoclinic
space group	$P2_1/n$ (C_{2h}^5, No. 14)	$P\bar{1}$ (C_i^1, No. 2)	$P2_1/n$ (C_{2h}^5, No. 14)
a, Å	14.166 (2)	13.596 (2)	15.666 (4)
b, Å	10.955 (2)	15.241 (2)	9.535 (2)
c, Å	15.007 (1)	11.765 (1)	16.335 (4)
α, deg	90	100.12 (1)	90
β, deg	100.95 (1)	98.52 (1)	102.55 (2)
γ, deg	90	100.66 (1)	90
V, Å^3	2286.5	2317.1	2381.7
Z	4	4	4
D_{calcd}, g cm^{-3}	1.304	1.344	1.570
$F(000)$	840	996	1140
T, K	295	295	295
μ, mm^{-1}	0.155	0.347	1.660
hkl range	$\pm h,+k,-l$	$\pm h,\pm k,-l$	$\pm h,+k,-l$
no. of data collcd	3338	6491	3882
no. of unique data	2979	6066	3116
R_{amal}[a]	0.024	0.018	0.023
no. of unique data used with $I \geq 2.5\sigma(I)$	2006	3087	2206
R	0.077	0.045	0.037
k	5.11	2.25	1
g	0.0005	0.0006	0.0076
R_w	0.086	0.051	0.040
residual ρ, e Å^{-3}	0.40	0.46	1.07

[a] $R_{amal} = \{\sum[N\sum[w(F_{mean} - |F_o|)^2]]/\sum[(N-1)\sum(w|F_o|^2)]\}^{1/2}$ 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 $[\sigma(F_o)]^{-2}$.

Determination and Refinement of Structures. The structures of the M = H_3O and K compounds were determined by direct methods (SHELX86),[20] and that of the M = Cs compound was solved from the interpretation of the Patterson map. A block-matrix least-squares procedure, based on F, was employed for the refinement of the M = K compound, and conventional full-matrix least-squares refinements were employed for the other compounds (SHELX76).[19] Anisotropic thermal parameters were employed for all non-H atoms, and H atoms were included in each model at their calculated positions. The C(23) atom in the M = H_3O structure was found to be disordered over two positions; these were refined with fractional site occupancies such that the sum = 1; at the conclusion of the refinement, the site occupancy for the C(23) atom was 0.634 (1). Similarly, two of the perchlorate O atoms, O(23) and O(24), were disordered, and these were refined as for the C(23) atom such that the final site occupancy for the major component was 0.548 (1). The location of three residual electron density peaks in the vicinity of the O(1) atom, consistent with the presence of three protons, confirmed the assignment of the cation as H_3O^+; the positions of these H atoms were included in the final refinement but were not refined. The crystallographic asymmetric unit for the M = K compound is composed of two independent $[K.C22C_5]ClO_4$ species, labeled molecules a and b, respectively. As for the M = H_3O compound, the perchlorate O atoms, O(23) and O(24) of molecule a, were found to be disordered, and these were refined as above such that the major component of the disorder had a fractional occupancy of 0.562 (1). A weighting scheme of the form $w = k/[\sigma^2(F) + |g|F^2]$ was introduced, and the refinements were continued until convergence; final refinement details are listed in Table I. The analysis of variance for each refinement showed no special features, indicating that an appropriate weighting scheme had been employed. No correction was applied for extinction in any of the refinements. The analysis of the M = H_3O compound was only of limited accuracy owing to the difficulty of obtaining suitable crystals; the results reported herein are the best of three data collections (including one measured at 200 K).

Fractional atomic coordinates are listed in Tables II–IV, and the numbering schemes employed are shown in Figures 1–3, which were drawn with the ORTEP[21] program at 25% probability ellipsoids. Selected geometric parameters are listed in Tables V–VII and, as for the diagrams, include only the major components of the disordered atoms where appropriate. Scattering factors for K^+ and Cs^+ (corrected for f' and f'')

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Table II. Fractional Atomic Coordinates (×10^4) for [$H_3O.C22C_5$]ClO_4

atom	*x*	*y*	*z*
O(1)	6605 (2)	2533 (3)	3233 (2)
N(1)	8458 (3)	2205 (4)	4783 (3)
C(2)	8949 (4)	1211 (6)	4412 (5)
C(3)	8402 (4)	47 (6)	4266 (5)
O(4)	7553 (3)	230 (3)	3597 (3)
C(5)	6998 (4)	–844 (5)	3408 (5)
C(6)	6093 (5)	–541 (5)	2809 (4)
O(7)	5530 (3)	168 (3)	3297 (3)
C(8)	4752 (5)	784 (6)	2743 (5)
C(9)	4253 (4)	1551 (6)	3254 (6)
N(10)	4808 (3)	2487 (4)	3827 (3)
C(11)	4349 (5)	3650 (6)	3620 (7)
C(12)	4843 (5)	4516 (6)	3178 (6)
O(13)	5711 (3)	4874 (3)	3755 (3)
C(14)	6328 (5)	5570 (5)	3337 (5)
C(15)	7251 (5)	5692 (5)	3998 (5)
O(16)	7736 (3)	4547 (3)	4065 (3)
C(17)	8480 (5)	4453 (6)	4840 (5)
C(18)	9037 (4)	3307 (6)	4780 (5)
C(19)	8254 (4)	1922 (6)	5668 (4)
C(20)	7179 (5)	1563 (6)	5653 (4)
C(21)	6561 (5)	2632 (6)	5534 (4)
C(22)	5453 (5)	2285 (6)	5487 (5)
C(23)	4905 (6)	1771 (8)	4758 (5)
C(23')[a]	4866 (9)	2902 (10)	4834 (9)
Cl(1)	1591 (1)	2374 (1)	3460 (1)
O(21)	1947 (5)	3385 (7)	3081 (6)
O(22)	1883 (5)	1400 (7)	2992 (6)
O(23)	2353 (6)	2185 (7)	4204 (5)
O(23')[b]	1584 (11)	2452 (9)	4335 (7)
O(24)	846 (6)	2315 (12)	3627 (8)
O(24')[b]	609 (6)	2423 (7)	2984 (8)

[a] Atom has site occupancy factor = 0.634 (1); see Experimental Section.
[b] Atom has site occupancy factor = 0.548 (1).

were from the literature,[22] while those for the remaining atoms were those incorporated in SHELX76.[19]

Solution Studies. Potentiometric titrations in water were carried out using a Metrohm E665 Dosimat autoburet interfaced to a Laser XT/3-8086 PC in conjunction with an Orion SA720 potentiometer and an Orion Ross Sureflow 81-72 BN combination electrode. All titrations were performed at 298.2 ± 0.1 K in a water-jacketed vessel which was closed apart from a vent to allow egress of nitrogen. A stream of nitrogen was bubbled 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 cm^3) from the autoburet against 0.004 mol dm^3 $HClO_4$ (10.00 cm^3) to determine E_0 and pK_w. (Under the conditions of these studies pK_w = 13.8.) The values of pK_{a1} = 11.43 ± 0.14 and pK_{a2} = 8.13 ± 0.10 for H_2C22C_5 (eqs 1 and 2) were determined by titration of solutions (10.00

$$K_{a1} = ([H^+][H.C22C_5^+])/[H_2.C22C_5^{2+}] \quad (1)$$

$$K_{a2} = ([H^+][C22C_5])/[H.C22C_5^+] \quad (2)$$

$$K = ([M.C22C_5^+])/([M^+][C22C_5]) \quad (3)$$

cm^3) 0.004, 0.001, and 0.010 mol dm^{-3} in $HClO_4$, $C22C_5$, and NEt_4ClO_4, respectively, with 0.100 mol dm^{-3} NEt_4OH. The apparent stability constants, *K* (eq 3), of [$M.C22C_5$]$^+$ (M^+ = Li^+, Na^+, K^+, Rb^+, Cs^+) were determined by titrating similar solutions containing $MClO_4$. For each metal ion, at least two titrations were performed, in which the metal ion:cryptand concentration ratio was varied. The *K* and pK_a values were determined using the program MINIQUAD.[23]

Table III. Fractional Atomic Coordinates (×10^4) for [$K.C22C_5$]ClO_4

atom	*x*	*y*	*z*
K(1)	2613 (1)	1738 (1)	656 (1)
K(2)	–2143 (1)	3358 (1)	7020 (1)
N(1a)	1807 (3)	165 (3)	–1576 (3)
C(2a)	2257 (4)	–602 (3)	–1325 (4)
C(3a)	2723 (4)	–479 (3)	–61 (4)
O(4a)	3585 (3)	250 (2)	176 (3)
C(5a)	4199 (4)	413 (3)	1310 (4)
C(6a)	5057 (4)	1192 (3)	1364 (5)
O(7a)	4665 (2)	1980 (2)	1296 (3)
C(8a)	5314 (4)	2652 (4)	876 (5)
C(9a)	4855 (4)	3464 (3)	865 (5)
N(10a)	3878 (3)	3302 (3)	36 (3)
C(11a)	3330 (4)	4029 (3)	338 (5)
C(12a)	2247 (4)	3836 (3)	–290 (5)
O(13a)	1714 (3)	3068 (2)	72 (3)
C(14a)	656 (4)	2857 (4)	–411 (5)
C(15a)	158 (4)	2054 (3)	59 (5)
O(16a)	590 (2)	1284 (2)	–210 (3)
C(17a)	230 (4)	774 (4)	–1365 (5)
C(18a)	719 (4)	–51 (3)	–1503 (5)
C(19a)	1921 (4)	357 (4)	–2737 (4)
C(20a)	3020 (5)	667 (4)	–2891 (5)
C(21a)	3673 (4)	1502 (4)	–2013 (5)
C(22a)	3303 (4)	2361 (4)	–2045 (5)
C(23a)	4036 (4)	3210 (4)	–1205 (5)
N(1b)	–4052 (3)	3517 (3)	5553 (4)
C(2b)	–4824 (4)	2742 (4)	5699 (5)
C(3b)	–4540 (4)	1843 (4)	5380 (5)
O(4b)	–3659 (3)	1826 (3)	6168 (3)
C(5b)	–3367 (5)	980 (3)	6034 (5)
C(6b)	–2423 (5)	1062 (4)	6937 (5)
O(7b)	–1580 (3)	1710 (2)	6814 (3)
C(8b)	–1066 (5)	1379 (4)	5926 (5)
C(9b)	–164 (4)	2117 (4)	5906 (5)
N(10b)	–445 (3)	2887 (3)	5464 (3)
C(11b)	394 (4)	3709 (4)	5863 (5)
C(12b)	267 (4)	4329 (4)	6955 (5)
O(13b)	–575 (3)	4712 (2)	6647 (3)
C(14b)	–691 (4)	5429 (3)	7540 (4)
C(15b)	–1613 (4)	5761 (3)	7075 (5)
O(16b)	–2475 (3)	5048 (2)	6952 (3)
C(17b)	–3379 (4)	5187 (4)	6333 (5)
C(18b)	–4204 (4)	4374 (4)	6226 (5)
C(19b)	–4083 (4)	3549 (4)	4289 (5)
C(20b)	–3024 (4)	3776 (4)	3976 (5)
C(21b)	–2473 (4)	2999 (4)	3944 (4)
C(22b)	–1384 (4)	3263 (4)	3720 (4)
C(23b)	–725 (4)	2665 (4)	4169 (4)
Cl(1a)	2265 (1)	1703 (1)	–6396 (2)
O(21a)	2991 (6)	2259 (7)	3200 (6)
O(22a)	1663 (7)	1311 (7)	4154 (7)
O(23a)	3026 (5)	1266 (5)	4021 (7)
O(23')[a]	2323 (7)	2510 (5)	4533 (7)
O(24a)	1894 (6)	1063 (6)	2508 (6)
O(24')[a]	1514 (7)	1937 (6)	2784 (8)
Cl(1b)	–2214 (1)	3493 (1)	–46 (1)
O(21b)	–1370 (3)	3929 (3)	–481 (4)
O(22b)	–2434 (3)	4090 (3)	897 (4)
O(23b)	–2004 (4)	2749 (3)	417 (5)
O(24b)	–3054 (3)	3253 (5)	–932 (4)

[a] Atom has site occupancy factor = 0.562 (1); see Experimental Section.

Stability constants for [$Ag.C22C_5$]$^+$ in methanol and dimethylformamide were determined through duplicate potentiometric titrations of 25 cm^3 of a 10^{-3} mol dm^{-3} $AgClO_4$ solution with a 10^{-2} mol dm^{-3} $C22C_5$ solution. Stability constants for the other cryptates were determined through duplicate competitive potentiometric titrations of 25 cm^3 of a 1.00 × 10^{-3} mol dm^{-3} $AgClO_4$ solution with solutions 5.00 × 10^{-2} mol dm^{-3} in both $LiClO_4$, $NaClO_4$, $KClO_4$, $CsClO_4$, or $TlClO_4$ and $C22C_5$ as described in the literature.[24] All titration solutions were 0.05 mol dm^{-3} in NEt_4ClO_4. The titrations were carried out under dry nitrogen in a water-jacketed (298.2 ± 0.1 K) titration vessel connected to a water-jacketed reference vessel by a salt bridge. For a given experiment, the titration and reference vessels and the salt bridge contained solutions were made up in the same solvent as that in the titration vessel and were

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(23) Sabatini, A.; Vacca, A.; Gans, P. *Talanta* **1974**, *21*, 53–77.

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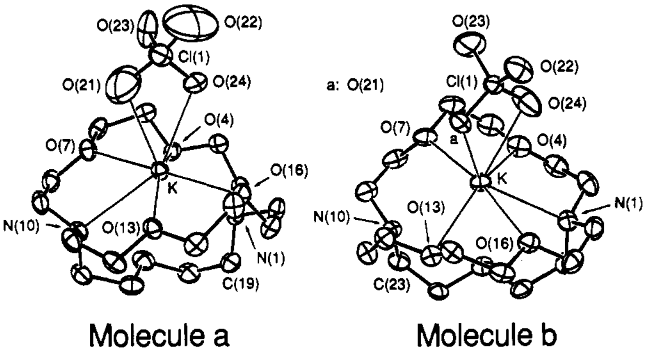
Table IV. Fractional Atomic Coordinates (×10^5 for Cs, ×10^4 for Others) for $[Cs.C22C_5]ClO_4$

atom	*x*	*y*	*z*
Cs	65181 (2)	36404 (4)	50451 (2)
N(1)	7478 (4)	684 (6)	5968 (3)
C(2)	7716 (5)	1200 (7)	6818 (4)
C(3)	8415 (5)	2307 (8)	6977 (4)
O(4)	8086 (3)	3556 (4)	6544 (3)
C(5)	8730 (5)	4615 (8)	6615 (5)
C(6)	8341 (5)	5894 (8)	6191 (5)
O(7)	8004 (3)	5711 (5)	5297 (3)
C(8)	8582 (6)	5984 (9)	4803 (6)
C(9)	8221 (6)	5627 (8)	3903 (5)
N(10)	8130 (3)	4121 (6)	3711 (3)
C(11)	7642 (5)	3846 (7)	2872 (5)
C(12)	6688 (5)	3524 (7)	2816 (4)
O(13)	6640 (3)	2243 (5)	3242 (3)
C(14)	5789 (4)	1719 (9)	3120 (5)
C(15)	5816 (5)	385 (9)	3596 (5)
O(16)	6063 (3)	669 (5)	4464 (3)
C(17)	6252 (6)	−510 (9)	4967 (5)
C(18)	6663 (5)	−104 (8)	5847 (5)
C(19)	8183 (6)	−161 (8)	5738 (5)
C(20)	8385 (5)	169 (9)	4914 (6)
C(21)	8743 (6)	1571 (8)	4832 (6)
C(22)	8940 (5)	1875 (8)	3977 (5)
C(23)	8997 (5)	3451 (8)	3826 (5)
Cl(1)	5051 (1)	3754 (2)	6684 (1)
O(21)	4195 (5)	3458 (8)	6411 (9)
O(22)	5632 (5)	2688 (7)	6650 (6)
O(23)	5278 (6)	4999 (9)	6327 (7)
O(24)	5128 (7)	4213 (17)	7467 (5)



Molecule a Molecule b

Figure 1. ORTEP plots of the structures of the two molecules in the asymmetric unit of $[K.C22C_5]ClO_4$ showing the atomic numbering.

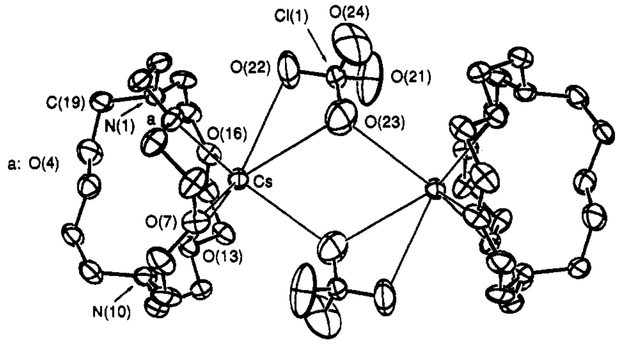


Figure 2. ORTEP plot of the structure of $[Cs.C22C_5]ClO_4$ showing the association between centrosymmetric molecules and the atomic numbering.

0.05 mol dm^{-3} in NEt_4ClO_4. The reference and titration electrodes were silver, and the reference solution was 10^{-2} mol dm^{-3} $AgClO_4$ in the chosen solvent.

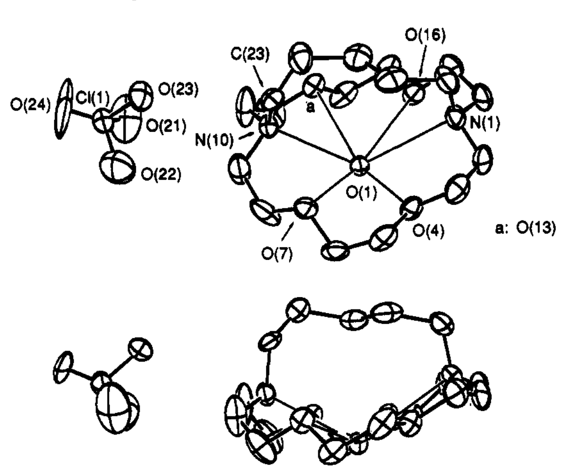


Figure 3. ORTEP plots of the structure of $[H_3O.C22C_5]ClO_4$ showing two views of the molecular structure and the atomic numbering.

Table V. Bond Distances (Å) for the $C22C_5$ cryptand in $[M.C22C_5]ClO_4$

atoms	M = H_3O	M = K molecule a	M = K molecule b	M = Cs
N(1)–C(2)	1.458 (7)	1.470 (7)	1.480 (7)	1.444 (8)
N(1)–C(18)	1.460 (7)	1.474 (6)	1.469 (7)	1.458 (9)
N(1)–C(19)	1.446 (7)	1.470 (7)	1.491 (7)	1.481 (8)
C(2)–C(3)	1.486 (8)	1.491 (7)	1.491 (9)	1.50 (1)
C(3)–O(4)	1.427 (7)	1.413 (5)	1.409 (7)	1.424 (7)
O(4)–C(5)	1.413 (6)	1.419 (6)	1.409 (7)	1.414 (8)
C(5)–C(6)	1.458 (8)	1.487 (7)	1.511 (8)	1.47 (1)
C(6)–O(7)	1.414 (6)	1.411 (7)	1.412 (7)	1.450 (9)
O(7)–C(8)	1.419 (7)	1.430 (7)	1.413 (7)	1.363 (9)
C(8)–C(9)	1.414 (9)	1.486 (8)	1.508 (8)	1.50 (1)
C(9)–N(10)	1.467 (7)	1.480 (6)	1.455 (8)	1.471 (9)
N(10)–C(11)	1.438 (7)	1.467 (7)	1.481 (6)	1.440 (9)
N(10)–C(23)	1.586 (9)	1.493 (7)	1.477 (6)	1.476 (9)
C(11)–C(12)	1.42 (1)	1.498 (7)	1.508 (7)	1.51 (1)
C(12)–O(13)	1.419 (7)	1.424 (6)	1.407 (7)	1.416 (8)
O(13)–C(14)	1.396 (7)	1.421 (6)	1.425 (6)	1.397 (8)
C(14)–C(15)	1.489 (9)	1.517 (8)	1.502 (8)	1.49 (1)
C(15)–O(16)	1.425 (6)	1.416 (6)	1.413 (6)	1.412 (8)
O(16)–C(17)	1.417 (7)	1.408 (6)	1.404 (7)	1.385 (9)
C(17)–C(18)	1.495 (8)	1.522 (8)	1.483 (7)	1.49 (1)
C(19)–C(20)	1.569 (9)	1.529 (8)	1.532 (8)	1.48 (1)
C(20)–C(21)	1.453 (8)	1.524 (7)	1.512 (9)	1.47 (1)
C(21)–C(22)	1.602 (9)	1.491 (9)	1.535 (8)	1.52 (1)
C(22)–C(23)	1.339 (9)	1.557 (7)	1.497 (9)	1.53 (1)

Results and Discussion

Crystal Structures of $[M.C22C_5]ClO_4$. An earlier crystal structure determination of $[Na.C22C_5]ClO_4$ shows that Na^+ forms close interactions with the four cryptand oxygen atoms (O(4)···Na = 2.394 (4), O(7)···Na = 2.453 (4), O(13)···Na = 2.417 (4), O(16)···Na = 2.481 (3) Å) and lies slightly below the mean plane formed by O(4), O(7), O(13), and O(16) (Table VIII).[14] The cryptand nitrogens do not interact significantly with Na^+, as indicated by Na···N(1) and Na···N(10) distances of 3.003 (5) and 3.025 (5) Å, respectively, and are 1.060 (3) and 2.203 (3) Å below the mean plane of the cryptand oxygens. The fifth coordination site about Na^+ is occupied by O(21), at 2.437 (4) Å, of ClO_4^-, such that Na^+ exists in an approximately square pyramidal coordination environment in the solid state. In molecule a of $[K.C22C_5]ClO_4$, K^+ lies 0.369 (1) Å above the mean plane of the four cryptand oxygens (Table VIII) with which it has close interactions of K···O(4) = 2.844 (4) Å, K···O(7) = 2.718 (3) Å, K···O(13) = 2.689 (4) Å, and K···O(16) = 2.701 (3) Å (Table VII and Figure 1). However, the cryptand oxygens O(4) and O(13) are respectively 0.257 (3) and 0.239 (3) Å below the mean plane and O(7) and O(16) are respectively 0.257 (4) and 0.252 (4) Å above, in contrast to the almost coplanar cryptand oxygens of $[Na.C22C_5]ClO_4$. More distant interactions exist between K^+ and the two cryptand nitrogens (K···N(1) = 3.132 (4) Å, K···N(10) = 2.939 (4) Å) where N(1) and N(10) are respectively 1.581 (4) and 1.180 (4) Å below the mean plane of the cryptand oxygens. Two closer interactions occur between K^+ and two oxygens of the perchlorate anion (K···O(21) = 2.900 (5) Å, K···O(24) = 2.794 (5) Å). Thus K^+ may be described as six-coordinated

Table VI. Bond Angles (deg) for the C22C$_5$ Cryptand in [M.C22C$_5$]ClO$_4$

		M = K		
atoms	M = H$_3$O	molecule a	molecule b	M = Cs
C(2)–N(1)–C(18)	107.9 (5)	108.4 (4)	109.6 (4)	109.9 (5)
C(2)–N(1)–C(19)	112.6 (5)	112.5 (4)	111.5 (4)	112.3 (6)
C(18)–N(1)–C(19)	113.0 (5)	109.9 (4)	111.4 (5)	111.4 (6)
N(1)–C(2)–C(3)	115.1 (5)	113.0 (4)	113.0 (5)	115.6 (6)
C(2)–C(3)–O(4)	109.2 (4)	106.9 (4)	109.2 (4)	109.3 (5)
C(3)–O(4)–C(5)	112.7 (4)	115.5 (4)	114.8 (4)	112.4 (5)
O(4)–C(5)–C(6)	108.9 (4)	106.4 (4)	108.9 (4)	109.8 (6)
C(5)–C(6)–O(7)	108.8 (5)	108.9 (4)	113.3 (5)	113.4 (6)
C(6)–O(7)–C(8)	114.1 (5)	113.3 (4)	113.5 (4)	115.5 (6)
O(7)–C(8)–C(9)	112.2 (6)	109.4 (4)	108.6 (4)	112.4 (6)
C(8)–C(9)–N(10)	117.8 (5)	115.0 (4)	113.6 (5)	115.5 (6)
C(9)–N(10)–C(11)	108.8 (5)	110.9 (4)	110.7 (4)	112.8 (5)
C(9)–N(10)–C(23)	96.8 (5)	111.4 (4)	110.9 (4)	110.6 (6)
C(11)–N(10)–C(23)	126.1 (6)	110.8 (4)	110.5 (4)	109.1 (6)
N(10)–C(11)–C(12)	116.8 (6)	115.0 (4)	112.8 (4)	114.2 (6)
C(11)–C(12)–O(13)	110.3 (6)	106.9 (4)	107.5 (4)	107.7 (5)
C(12)–O(13)–C(14)	114.9 (5)	112.0 (4)	114.0 (3)	113.0 (6)
O(13)–C(14)–C(15)	107.2 (5)	107.8 (4)	107.3 (4)	108.3 (6)
C(14)–C(15)–O(16)	108.6 (5)	112.3 (5)	107.7 (4)	109.4 (6)
C(15)–O(16)–C(17)	113.3 (5)	113.8 (4)	114.7 (4)	114.6 (6)
O(16)–C(17)–C(18)	109.3 (5)	107.7 (4)	108.8 (5)	110.6 (6)
C(17)–C(18)–N(1)	113.0 (5)	114.2 (4)	115.4 (5)	116.4 (6)
N(1)–C(19)–C(20)	113.9 (5)	115.1 (4)	113.3 (4)	115.7 (6)
C(19)–C(20)–C(21)	111.1 (6)	117.1 (5)	113.5 (5)	115.9 (7)
C(20)–C(21)–C(22)	112.1 (6)	114.3 (5)	112.7 (5)	114.5 (7)
C(21)–C(22)–C(23)	123.2 (7)	112.7 (5)	111.6 (5)	111.5 (6)
C(22)–C(23)–N(10)	116.8 (6)	112.6 (4)	111.9 (4)	111.2 (6)

Table VII. Geometric Parameters (Å, deg) for the M Cations in [M.C22C$_5$]ClO$_4$

	M = H$_3$O		
O(1)···O(4)	2.862 (5)	O(1)···O(7)	3.016 (5)
O(1)···O(13)	3.028 (5)	O(1)···O(16)	2.869 (5)
O(1)···N(1)	3.180 (5)	O(1)···N(10)	2.853 (5)
O(4)···O(1)···O(7)	57.2 (2)	O(4)···O(1)···O(13)	154.3 (2)
O(4)···O(1)···O(16)	113.1 (2)	O(4)···O(1)···N(1)	57.9 (2)
O(4)···O(1)···N(10)	109.8 (2)	O(7)···O(1)···O(13)	118.7 (2)
O(7)···O(1)···O(16)	152.9 (2)	O(7)···O(1)···N(1)	103.4 (2)
O(7)···O(1)···N(10)	59.3 (2)	O(13)···O(1)···O(16)	57.5 (2)
O(13)···O(1)···N(1)	103.5 (2)	O(13)···O(1)···N(10)	59.5 (2)
O(16)···O(1)···N(1)	56.9 (2)	O(16)···O(1)···N(10)	109.6 (2)
N(1)···O(1)···N(10)	115.5 (2)		
	M = K (Molecule a)		
K···O(4)	2.844 (4)	K···O(7)	2.718 (3)
K···O(13)	2.689 (4)	K···O(16)	2.701 (3)
K···N(1)	3.132 (4)	K···N(10)	2.939 (4)
K···O(21)	2.900 (5)	K···O(24)	2.794 (5)
O(4)···K···O(7)	59.5 (1)	O(4)···K···O(13)	154.0 (1)
O(4)···K···O(16)	112.8 (1)	O(4)···K···N(10)	106.3 (1)
O(4)···K···O(21)	104.5 (1)	O(4)···K···O(24)	90.7 (1)
O(7)···K···O(13)	122.7 (1)	O(7)···K···O(16)	171.7 (1)
O(7)···K···N(10)	63.0 (1)	O(7)···K···O(21)	75.7 (1)
O(7)···K···O(24)	102.7 (1)	O(13)···K···O(16)	62.6 (1)
O(13)···K···N(10)	62.0 (1)	O(13)···K···O(21)	100.8 (1)
O(13)···K···O(24)	112.4 (1)	O(16)···K···N(10)	119.4 (1)
O(16)···K···O(21)	110.5 (1)	O(16)···K···O(24)	79.7 (1)
N(10)···K···O(21)	101.8 (1)	N(10)···K···O(24)	144.3 (1)
O(21)···K···O(24)	42.8 (1)		
	M = K (Molecule b)		
K···O(4)	2.736 (3)	K···O(7)	2.739 (4)
K···O(13)	2.822 (4)	K···O(16)	2.710 (4)
K···N(1)	2.971 (4)	K···N(10)	3.256 (4)
K···O(21)	2.890 (4)	K···O(24)	2.883 (4)
O(4)···K···O(7)	63.0 (1)	O(4)···K···O(13)	150.2 (1)
O(4)···K···O(16)	121.6 (1)	O(4)···K···N(1)	61.3 (1)
O(4)···K···O(21)	119.9 (1)	O(4)···K···O(24)	79.6 (1)
O(7)···K···O(13)	110.7 (1)	O(7)···K···O(16)	169.8 (1)
O(7)···K···N(1)	120.0 (1)	O(7)···K···O(21)	95.0 (1)
O(7)···K···O(24)	96.9 (1)	O(13)···K···O(16)	60.5 (1)
O(13)···K···N(1)	106.4 (1)	O(13)···K···O(21)	89.0 (1)
O(13)···K···O(24)	129.9 (1)	O(16)···K···N(1)	61.6 (1)
O(16)···K···O(21)	90.0 (1)	O(16)···K···O(24)	93.1 (1)
N(1)···K···O(21)	131.4 (1)	N(1)···K···O(24)	93.7 (1)
O(21)···K···O(24)	46.3 (1)		
	M = Cs		
Cs···O(4)	3.069 (4)	Cs···O(7)	3.012 (5)
Cs···O(13)	3.275 (4)	Cs···O(16)	3.023 (5)
Cs···N(1)	3.395 (5)	Cs···N(10)	3.703 (5)
Cs···O(22)	3.348 (8)	Cs···O(23)	3.407 (5)
Cs···O(23)′ [a]	3.447 (5)		
O(4)···Cs···O(7)	56.5 (1)	O(4)···Cs···O(13)	120.9 (1)
O(4)···Cs···O(16)	108.6 (1)	O(4)···Cs···O(22)	76.4 (1)
O(4)···Cs···O(23)	89.1 (1)	O(4)···Cs···O(23)′	158.0 (1)
O(7)···Cs···O(13)	101.3 (1)	O(7)···Cs···O(16)	141.2 (1)
O(7)···Cs···O(22)	120.7 (1)	O(7)···Cs···O(23)	101.2 (1)
O(7)···Cs···O(23)′	109.9 (1)	O(13)···Cs···O(16)	52.6 (1)
O(13)···Cs···O(22)	135.2 (1)	O(13)···Cs···O(23)	149.3 (1)
O(13)···Cs···O(23)′	76.5 (1)	O(16)···Cs···O(22)	83.2 (1)
O(16)···Cs···O(23)	115.0 (1)	O(16)···OCs···O(23)′	92.6 (1)
O(22)···Cs···O(23)	39.9 (1)	O(22)···Cs···O(23)′	101.1 (1)
O(23)···Cs···O(23)′	76.3 (1)		

[a] Primed atom related by center of inversion.

if the six oxygen interactions only are considered and eight-coordinate if the two nitrogen interactions are included. Molecule b in [K.C22C$_5$]ClO$_4$ has a similar structure (Tables V–VIII and Figure 1).

In [Cs.C22C$_5$]ClO$_4$, Cs$^+$ lies 1.2996 (3) Å above the mean plane of the four cryptand oxygens (Table VIII) with which it has close interactions of Cs···O(4) = 3.069 (4) Å, Cs···O(7) = 3.012 (5) Å, Cs···O(13) = 3.275 (4) Å, and Cs···O(16) = 3.023 (5) Å (Table VII and Figure 2). The cryptand oxygens O(4) and O(13) are respectively 0.263 (5) and 0.257 (4) Å below the mean plane, and O(7) and O(16) are respectively 0.319 (5) and 0.318 (4) Å above the mean plane (Table VIII and Figure 2). More distant interactions exist between Cs$^+$ and the two cryptand nitrogens (Cs···N(1) = 3.395 (5) Å, Cs···N(10) = 3.703 (5) Å) where N(1) and N(10) are respectively 0.988 (6) and 1.242 (5) Å below the mean plane of the cryptand oxygens. Interactions also occur between Cs$^+$ and two perchlorate anions (Cs···O(22) = 3.348 (8) Å, Cs···O(23) = 3.407 (5) Å, Cs···O(23′) = 3.447 (5) Å; the primed atom is related by a crystallographic center of inversion). Thus Cs$^+$ may be described as seven-coordinated if only the seven oxygen interactions are considered and nine-coordinate if the two nitrogen interactions are included. As can be seen from Figure 2, O(23) of the ClO$_4^-$ anion "bridges" two Cs$^+$ cations, leading to a loosely associated dimer in the crystalline state. The remaining interatomic distances and angles for [Cs.C22C$_5$]ClO$_4$ and also for [K.C22C$_5$]ClO$_4$ are as anticipated and do not merit further discussion.

From these data it is seen that there is a general trend in the structure of [M.C22C$_5$]ClO$_4$ where M$^+$ moves further out of the plane of the cryptand oxygens as the size of M$^+$ increases and the cryptand oxygens depart from coplanarity with increasing size of M$^+$. By comparison the four cryptand oxygens in [H$_3$O.C22C$_5$]ClO$_4$ are coplanar to within ±0.019 (4) Å, with the H$_3$O$^+$ oxygen positioned 0.666 (3) Å above this plane. In all four of the [M.C22C$_5$]ClO$_4$ species, the cryptand is in the endo-endo conformation, where the lone pairs of electrons of the nitrogens are directed toward the center of the cryptand cavity.

In [K.C22]SCN the four oxygens and K$^+$ are coplanar (K···O distances = 2.830 (3) Å) with the macrocylic nitrogens (K···N distances = 2.856 (3) Å), respectively 0.64 Å above and below this plane.[12] The interaction with SCN$^-$ is characterized by K···N and K···S distances of 3.33 (1) Å, and if these interactions are included, K$^+$ is eight-coordinated. This provides an interesting comparison with [K.C22C$_5$]ClO$_4$ and indicates that the –(CH$_2$)$_5$– linkage joining the cryptand nitrogens prevents the 4,7,13,16-tetraoxa-1,10-diazacyclooctadecane ring of C22C$_5$ from assuming a conformation which can accommodate K$^+$ in the plane of the four oxygens. As Na$^+$ is almost coplanar with the cryptand oxygens in [Na.C22C$_5$]ClO$_4$, it appears that conformational constraints restrict the effective radius of the ring delineated by these oxygens to ≥1.02 Å but ≤1.38 Å.

Table VIII. Distances (Å) of M, O(4), O(7), O(13), and O(16) from the Mean Plane of the Cryptand Oxygens in $[M.C22C_5]ClO_4$

	dist Å from mean plane of O(4), O(7), O(13), and O(16)						
M^+	M	O(4)	O(7)	O(13)	O(16)	N(1)	N(10)
$Na^{+\,a}$	−0.011 (2)	0.077 (3)	−0.088 (3)	0.089 (3)	−0.078 (3)	−1.060 (3)	−2.203 (3)
K^+ (molecule a)	0.369 (1)	−0.257 (3)	0.257 (4)	−0.239 (3)	0.252 (4)	−1.581 (4)	−1.180 (4)
K^+ (molecule b)	0.441 (1)	−0.295 (4)	0.286 (4)	−0.234 (3)	0.255 (4)	−1.110 (4)	−1.472 (4)
Cs	1.2996 (3)	−0.263 (5)	0.319 (5)	−0.257 (4)	0.318 (4)	−0.988 (6)	−1.242 (5)
H_3O^+	0.666 (3)	0.017 (4)	−0.017 (4)	0.017 (4)	−0.019 (4)	−1.254 (4)	−0.642 (5)

[a] Reference 8. It should be noted that the mean plane of Na, O(4), O(7), O(13), and O(16) is discussed in ref 8 and that the mean plane of O(4), O(7), O(13), and O(16) calculated from the data in that reference is discussed here.

Table IX. Apparent Stability Constants of $[M.C221]^+$, $[M.C22C_5]^+$, $[M.C22C_2]^+$, and $[M.C22]^+$ in Four Solvents at 298.2 K

	log (K/dm^3 mol^{-1})			
species^a	methanol (D_N = 19.0^b or 23.5^c)	dimethylformamide (D_N = 26.6^b)	water (D_N = 18.0^b or 33.0^c)	acetonitrile (D_N = 14.1^b)
$[Li.C221]^{+\,d}$	5.38	3.58	2.50	10.33
$[Na.C221]^{+\,d}$	8.65	7.93	5.4	>11.3
$[K.C221]^{+\,d}$	8.54	6.66	3.95	9.5
$[Rb.C221]^{+\,d}$	6.74	5.35	2.55	7.27
$[Cs.C221]^{+\,d}$	4.33	3.61	<2.0	5.15
$[Tl.C221]^{+\,e}$	10.75	8.61	6.8	11.92
$[Ag.C221]^{+\,f}$	14.64	12.41	10.6	11.24
$[Li.C22C_5]^{+\,f}$	2.30 ± 0.21	2.21 ± 0.18	2.08 ± 0.10	6.07 ± 0.04
$[Na.C22C_5]$	5.41 ± 0.06^g	3.66 ± 0.06^g	2.58 ± 0.04^f	7.55 ± 0.13^f
$[K.C22C_5]^{+\,f}$	5.8 ± 0.3	3.85 ± 0.14	3.41 ± 0.11	
$[Rb.C22C_5]^{+\,f}$	5.7 ± 0.2	3.82 ± 0.13	3.28 ± 0.07	
$[Cs.C22C_5]^{+\,f}$	4.8 ± 0.2	2.90 ± 0.13	3.31 ± 0.11	
$[Tl.C22C_5]^{+\,f}$	6.48 ± 0.14	5.05 [illegible] 0.15	4.10 ± 0.02	
$[Ag.C22C_5]^{+\,f}$	11.13 ± 0.12	9.40 ± 0.13	9.31 ± 0.05	8.27 ± 0.02
$[Li.C22C_2]^{+\,h}$	4.0	3.5	<2	7.8
$[Na.C22C_2]^{+\,i}$	6.6	6.1	3.2	9.4
$[K.C22C_2]^{+\,i}$		3.2	<2	7.2
$[Cs.C22C_2]^{+\,i}$		2.7	<2	5.0
$[Tl.C22C_2]^{+\,i}$	7.8	6.7		10.4
$[Ag.C22C_2]^{+\,i}$	10.2	9.4	6.0	9.4
$[Li.C22]^+$		~0.0^j		4.39^j
$[Na.C22]^+$	1.0^k			4.49,^{l} 4.30^m
$[K.C22]^+$	2.04^n			4.35,^{l} 4.32^m
$[Rb.C22]^+$	1.2^k			3.37^m
$[Cs.C22]^+$		0.61^j		2.25,^{l} 2.48^m
$[Tl.C22]^+$	3.54^o	3.41,^{o} 3.22^j	1.1^p	6.82^o
$[Ag.C22]^+$	9.99^o	9.91^o	8.08^m	7.94^o

[a] Respective six- and eight-coordinate ionic radii (Å) from ref 11: Li^+ = 0.76, 0.92; Na^+ = 1.02, 1.18, K^+ = 1.38, 1.51; Rb^+ = 1.52, 1.61; Cs^+ = 1.67, 1.74; Tl^+ = 1.50, 1.59; Ag^+ = 1.15, 1.28. [b,c] Gutmann donor number from ref 25 and from refs 26 and 27, respectively. It has been suggested that the D_N values of 23.5 and 33.0 obtained in bulk solvent are more appropriate for methanol and water solutions rather than D_N = 19.0 and 18.0 obtained in 1,2-dichloroethane solution, where the hydrogen-bonding interactions are disrupted. [d] Reference 6 and references therein. [e] Cox, B. G.; Stroka, J.; Schneider, I.; Schneider, H. *J. Chem. Soc., Faraday Trans. 1* **1989**, *85*, 187–198. [f] This work—errors represent one standard deviation. [g] Reference 8. [h] Reference 9. [i] Reference 10. [j] Reference 13. [k] Reference 1. [l] Reference 14. [m] Reference 15. [n] Reference 16. [o] Cox, B. G.; Firman, P.; Horst, H.; Schneider, H. *Polyhedron* **1983**, *2*, 343–347. [p] Anderegg, G. *Helv. Chim. Acta* **1975**, *58*, 1218–1225.

Solution Stability Studies. The apparent stability constants (K) for $[M.C22C_5]^+$ appear in Table IX, from which it is seen that the variation of stability is $Li^+ < Na^+ < K^+ \geq Rb^+ \geq Cs^+$ in methanol, dimethylformamide, and water, and that stability generally decreases 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,[25] where the second values 23.5 and 33.0 quoted for methanol and water in Table IX are probably the most appropriate, as they pertain to bulk solvent, whereas the values of 19.0 and 18.0 arise from studies in 1,2-dichloroethane, where intermolecular hydrogen bonding in protic solvents is disrupted.[26,27]) This influence of the solvent is also observed for $[Ag.C22C_5]^+$ and $[Tl.C22C_5]^+$. The particularly high stability of $[Ag.C22C_5]^+$ may be attributed to the soft-acid nature of Ag^+ and its consequently greater ability to bond with the cryptand nitrogens.[28,29] However, in acetonitrile the stabilities of the alkali metal cryptates more closely approach those of the silver(I) cryptates, as this nitrogen donor solvent competes more effectively for Ag^+ than for the alkali metal ions. Thallium(I) is intermediate between the alkali metal ions and Ag^+ in soft/hard-acid character and as a consequence also bonds more strongly with nitrogen donor atoms than does Rb^+, which it most resembles in ionic radius (Table IX), but less strongly than does Ag^+.

The variation in stability of $[M.C221]^+$ and $[M.C22C_2]^+$ is $Li^+ < Na^+ > K^+ > Cs^+$, which contrasts with the variation $Li^+ < Na^+ < K^+ \geq Rb^+ \geq Cs^+$ exhibited by $[M.C22C_5]^+$. The observation that $[Na.C221]^+$ is the most stable of the alkali metal $[M.C221]^+$ cryptates suggests that Na^+ occupies the center of the C221 cavity and achieves optimum bonding distances and is substantially isolated from solvent interaction, while Li^+ and K^+ are respectively too small and too large to achieve optimum bonding distances. This is consistent with cryptate structures determined in the solid state, where Na^+ occupies the center of the cryptand in *inclusive* $[Na.C221]^+$ and K^+ sits on the tetraoxa face of the cryptand in *exclusive* $[K.C221]^+$.[5] (The cavity radii[2] of $C22C_5$ and C221 are ca. 1.10 Å, which closely approximates the radius of Na^+ (Table IX).)

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In contrast, $[Na.C22C_5]^+$ is less stable than $[K.C22C_5]^+$ in solution, and Na^+ and K^+ are respectively 0.011 (2) Å and 0.369 (1)–0.441 (1) Å below and above the common plane of the four cryptand oxygens in the solid state. This, together with the observation that $[Na.C22C_5]^+$ and $[K.C22C_5]^+$ are less stable than their C221 analogues in solution, illustrates the effect of the replacement of the fifth oxygen donor atom of C221 by a methylene moiety in $C22C_5$. Thus, the overall electrostatic interactions between $C22C_5$ and Na^+ and K^+ are decreased by comparison with those between C221 and these ions, and the balance of the electrostatic field of the donor atoms of $C22C_5$ and that of ClO_4^- is such that in the solid state Na^+ is only in bonding distance of the four cryptand oxygen atoms, with which it is almost coplanar, despite the comparable sizes of the $C22C_5$ cavity and Na^+. (It is assumed that, in solution, the solid-state $[M.C22C_5]^+$ structures are largely retained, with the interactions between M^+ and ClO_4^- being replaced by solvent interactions). Evidently, the balance between the electrostatic interactions of M^+ with the cryptand and the solvent (where solvation energy decreases from Li^+ to Cs^+) results in $[K.C22C_5]^+$ and $[Rb.C22C_5]^+$ being the most stable of the alkali metal ion $C22C_5$ cryptates.

An interesting comparison may be made with the $[M.C22C_2]^+$ cryptates, where, in 4,7,13,16-tetraoxa-1,10-diazabicyclo[8.8.2]eicosane, $C22C_2$, the cavity size is contracted by comparison to that in $C22C_5$, through the replacement of the $>N(CH_2)_5N<$ moiety by $>N(CH_2)_2N<$ (Chart I). The stabilities of the $[M.C22C_2]^+$ cryptates vary in the sequence $Li^+ < Na^+ > K^+ > Cs^+$ (Table IX), coincident with the angle between the planes delineated by the oxygens of each of the $-(CH_2)_2O(CH_2)_2O(CH_2)_2-$ moieties and the two nitrogen atoms varying in the sequence 70.9, 89.6, and 100° for Li^+, Na^+, and K^+, respectively. As the corresponding angle is 88.4° in free $C22C_2$, the greater stability of $[Na.C22C_2]^+$ is predominantly attributable to a minimization of strain in this cryptate.

The cryptands C221, $C22C_5$, and $C22C_2$ may be viewed as modifications of 4,7,13,16-tetraoxa-1,10-diazacyclooctadecane in which the amine hydrogens have been displaced by a $-(CH_2)_2O(CH_2)_2-$, a $-(CH_2)_5-$, and a $-(CH_2)_2-$ bridge between the two nitrogens, respectively. The overall effect of these bridges is to decrease the flexibility of the 4,7,13,16-tetraoxa-1,10-diazacyclooctadecane ring by comparison to that of C22, with the result that the more rigid $[M.C22C_5]^+$ and $[M.C22C_2]^+$ cryptates are more stable than $[M.C22]^+$, which has the same number and type of donor atoms. This indicates that the exclusion of solvent from approaching one side of the metal ion in $[M.C22C_5]^+$ and $[M.C22C_2]^+$, resulting from the structure of these cryptates, combined with relative inflexibility of the corresponding cryptands, increases stability by comparison with that of $[M.C22]^+$, whose structure and greater C22 flexibility render the metal ion more accessible to solvent.

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Supplementary Material Available: Tables giving anisotropic thermal parameters, hydrogen atom parameters, bond distances, and bond angles (12 pages); listings of structure factors (23 pages). Ordering information is given on any current masthead page.