

Complexation of Alkali Metal Ions by the Pendant Arm Macrocyclic Ligand 1,4,7,10-Tetrakis(2-hydroxyethyl)-1,4,7,10-tetraazacyclododecane. A Potentiometric Titration and Nuclear Magnetic Resonance Study

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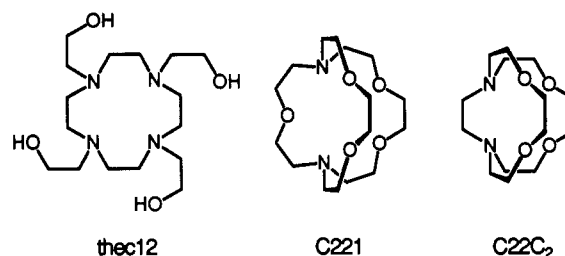
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Complexation of Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺, and Ag⁺ by the pendant arm macrocyclic ligand 1,4,7,10-tetrakis(2-hydroxyethyl)-1,4,7,10-tetraazacyclododecane (thec12) has been studied in methanol and dimethylformamide. A substantial variation in the stability of [M(thec12)]⁺ occurs as M⁺ is varied in the sequence Li⁺ (3.09 ± 0.06 and 2.99 ± 0.12), Na⁺ (4.53 ± 0.06 and 3.37 ± 0.06), K⁺ (2.43 ± 0.08 and 1.59 ± 0.11), Rb⁺ (2.20 ± 0.10 and 1.39 ± 0.09), Cs⁺ (1.90 ± 0.10 and 1.23 ± 0.08), and Ag⁺ (12.57 ± 0.04 and 11.16 ± 0.05), where the figures in parentheses are log (K/dm³ mol⁻¹) and K represents the apparent stability constants of [M(thec12)]⁺ in methanol and dimethylformamide, respectively, determined by potentiometric titration at 298.2 K. For [Li(thec12)]⁺ and [Na(thec12)]⁺ the monomolecular decomplexation processes in methanol are characterized by $k_d(298.2\text{ K}) = 729 \pm 17$ and $209 \pm 3\text{ s}^{-1}$, $\Delta H_d^\ddagger = 38.0 \pm 0.7$ and $68.3 \pm 1.4\text{ kJ mol}^{-1}$, and $\Delta S_d^\ddagger = -62.8 \pm 1.2$ and $28.4 \pm 0.8\text{ J K}^{-1}\text{ mol}^{-1}$, respectively, determined by ⁷Li and ²³Na NMR spectroscopy. The analogous parameters determined in dimethylformamide are $k_d(298.2\text{ K}) = 587 \pm 31$ and $299 \pm 7\text{ s}^{-1}$, $\Delta H_d^\ddagger = 41.8 \pm 0.7$ and $56.4 \pm 0.7\text{ kJ mol}^{-1}$, and $\Delta S_d^\ddagger = -51.9 \pm 3.3$ and $-8.4 \pm 2.4\text{ J K}^{-1}\text{ mol}^{-1}$. These data are compared with those obtained for other alkali metal complexes, which together demonstrate a range of different mechanisms through which selectivity occurs in alkali metal ion complexation.

Introduction

The selective complexation of alkali metal ions by cryptands, crown ethers, and similar ligands is well established,^{1–14} as is the complexation of di- and trivalent transition and main group metal ions by tetraaza and tetraaza pendant arm macrocycles.^{15–22} The

Chart I. Ligand Structures



ability of the latter type of ligand to complex alkali metal ions has been studied in the solid state,^{23,24} but there appear to be few quantitative studies of such complexation in solution. Accordingly we report an equilibrium and kinetic study of such complexation by 1,4,7,10-tetrakis(2-hydroxyethyl)-1,4,7,10-tetraazacyclododecane (thec12, whose structure is shown in Chart I) which is selective for Na⁺ in methanol and dimethylformamide. (These solvents were chosen as there is available a substantial amount of data obtained in them for systems with which to make comparisons). X-ray crystallographic studies of the Li⁺, Na⁺, and K⁺ complexes of thec12 show the metal ion to be bound by four nitrogens in each case and one, three, and four oxygens in the cases of Li⁺, Na⁺, and K⁺, respectively, where in [K(thec12)]⁺ the metal ion is completely encapsulated in the cavity formed by the eight coordinating ligand atoms in approximate square antiprismatic array.^{23,24} This study facilitates a comparison with complexes of the Na⁺ selective ligands 4,7,13,16,21-pentaoxa-1,10-diazabicyclo[8.8.5]tricosane, C221, which has a relatively rigid preformed cavity,^{10–12} and clam-like 4,7,13,16-tetraoxa-

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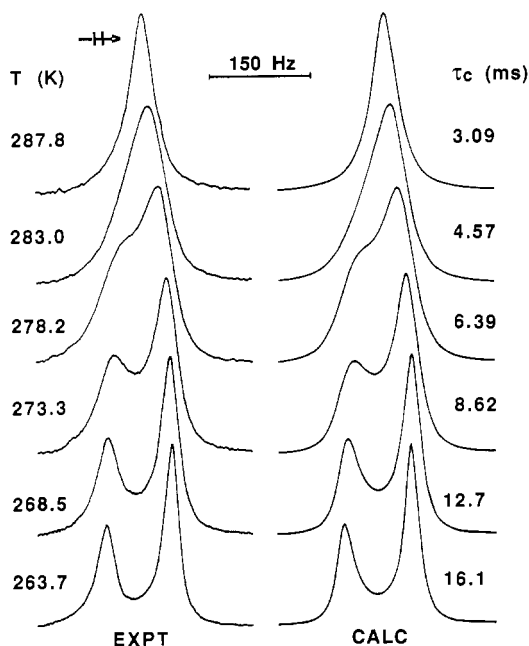


Figure 1. Typical exchange-modified 116.59-MHz ^7Li NMR spectra of a dimethylformamide solution of solvated Li^+ ($0.0196 \text{ mol dm}^{-3}$) and $[\text{Li}(\text{thecl2})]^+$ ($0.0295 \text{ mol dm}^{-3}$). Experimental temperatures and spectra appear to the left of the figure, and the best fit calculated line shapes and corresponding τ_c values appear to the right. The resonance of $[\text{Li}(\text{thecl2})]^+$ appears upfield from that of solvated Li^+ .

1,10-diazabicyclo[8.8.2]eicosane, $\text{C}_{22}\text{H}_{42}$, which can adjust the size of its cavity by varying the angle between its jaws.^{13,14}

Experimental Section

Thecl2 was prepared by a method similar to that in the literature.²⁵ Rubidium and cesium perchlorate were precipitated from solutions of their chlorides by the addition of concentrated perchloric acid and were recrystallized from water until chloride was absent. Potassium perchlorate (BDH) was recrystallized from water. Lithium and 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.

Methanol and dimethylformamide were purified and dried by literature methods,²⁶ and were stored under nitrogen over Linde 3- and 4-Å molecular sieves in the cases of methanol and dimethylformamide, respectively. The water content of these solvents was below the Karl Fischer detection level of approximately 50 ppm. Solutions of anhydrous metal perchlorates and thecl2 were prepared under dry nitrogen in a glovebox. For ^7Li and ^{23}Na NMR studies these solutions were degassed and sealed under vacuum in 5-mm NMR tubes which were 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.

^7Li and ^{23}Na NMR spectra were run at 116.59 and 79.39 MHz on a Bruker CXP-300 spectrometer. In the ^7Li 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 a 8000 Hz spectral width for each solution. The solution temperature was controlled to within $\pm 0.3 \text{ K}$ using a Bruker B-VT 1000 temperature controller. The Fourier transformed spectra were subjected to complete line shape analysis²⁷ on a VAX 11-780 computer to obtain kinetic data. The temperature dependent ^7Li and ^{23}Na line widths and chemical shifts employed in the lineshape analysis were obtained from a combination of extrapolation from low temperatures where no exchange induced modification occurred and from the line width and chemical shift variations of separate solutions containing either Li^+ , $[\text{Li}(\text{thecl2})]^+$, Na^+ , or $[\text{Na}(\text{thecl2})]^+$ as the only species.

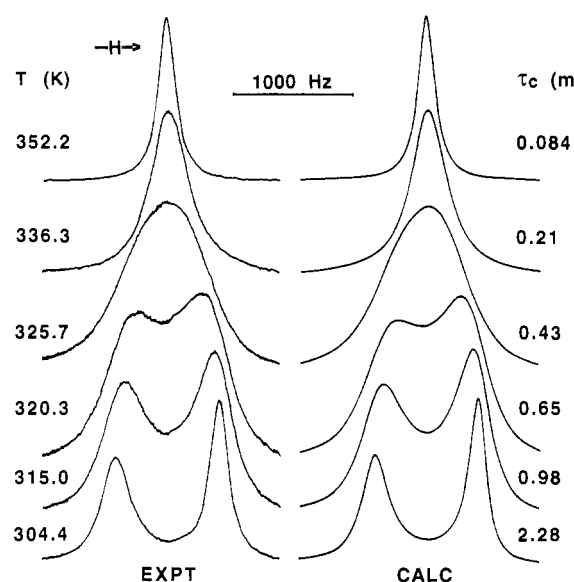


Figure 2. Typical exchange-modified 79.39-MHz ^{23}Na NMR spectra of a dimethylformamide solution of solvated Na^+ ($0.0250 \text{ mol dm}^{-3}$) and $[\text{Na}(\text{thecl2})]^+$ ($0.0250 \text{ mol dm}^{-3}$). Experimental temperatures and spectra appear to the left of the figure, and the best fit calculated line shapes and corresponding τ_c values appear to the right. The resonance of $[\text{Na}(\text{thecl2})]^+$ appears downfield from that of solvated Na^+ .

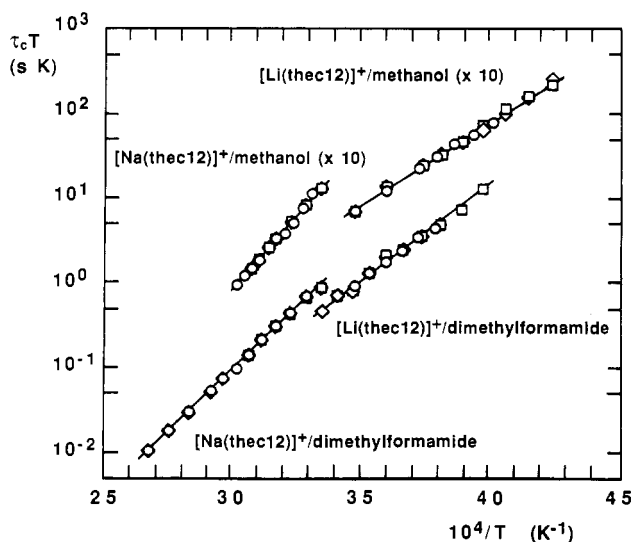


Figure 3. Temperature variations of τ_c for $[\text{Li}(\text{thecl2})]^+$ and $[\text{Na}(\text{thecl2})]^+$. Data points for each set of solutions i–iii are represented by diamonds, circles, and squares, respectively. The data sets obtained in methanol are multiplied by 10. The solid lines represent the best fits of the combined data for each group of solutions to eq 3.

Apparent stability constants (K , eq 1) for $[\text{Ag}(\text{thecl2})]^+$ were determined by duplicated potentiometric titrations of 20 cm^3 of $1.00 \times 10^{-3} \text{ mol dm}^{-3} \text{ AgClO}_4$ solution with a $1.00 \times 10^{-2} \text{ mol dm}^{-3} \text{ thecl2}$ solution. For $[\text{Li}(\text{thecl2})]^+$ and its Na^+ , K^+ , Rb^+ , and Cs^+ analogues, apparent stability constants were determined through duplicate competitive potentiometric titrations of 20 cm^3 of $1.00 \times 10^{-3} \text{ mol dm}^{-3} \text{ AgClO}_4$ solution with a solution $5.00 \times 10^{-2} \text{ mol dm}^{-3}$ in the appropriate alkali metal ion perchlorate and $1.00 \times 10^{-2} \text{ mol dm}^{-3} \text{ thecl2}$ as described in the literature.²⁸ Titrations were carried out under dry nitrogen in a thermostated ($298.2 \pm 0.1 \text{ K}$) titration vessel connected to a thermostated reference vessel by a salt bridge using silver wire titration and reference electrodes. 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 $1.00 \times 10^{-2} \text{ mol dm}^{-3}$ in AgClO_4 . All titration solutions and that in the salt bridge when used were 0.05 mol dm^{-3} in

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Table I. Variation of Stability of $[M(\text{thec12})]^+$ and Other Complexes with M^+ at 298.2 K

complex	solvent	$\log(K/\text{dm}^3 \text{ mol}^{-1})^a$					
		$M^+ = \text{Li}^+$	$M^+ = \text{Na}^+$	$M^+ = \text{K}^+$	$M^+ = \text{Rb}^+$	$M^+ = \text{Cs}^+$	$M^+ = \text{Ag}^+$
$[\text{M}(\text{thec12})]^+{}^b$	methanol	3.09 ± 0.06	4.53 ± 0.06	2.43 ± 0.08	2.20 ± 0.10	1.90 ± 0.10	12.57 ± 0.04
$[\text{M}(\text{thec12})]^+{}^b$	dimethylformamide	2.99 ± 0.12	3.37 ± 0.06	1.59 ± 0.11	1.39 ± 0.09	1.23 ± 0.08	11.16 ± 0.05
$[\text{M}(\text{C221})]^+{}^c$	methanol	5.38	8.65	8.54	6.74	4.33	14.64
$[\text{M}(\text{C221})]^+{}^c$	dimethylformamide	3.58	7.93	6.66	5.35	3.61	12.41
$[\text{M}(\text{C22C}_2)]^+{}^d$	methanol	4.0^d	6.6^e				10.2^d
$[\text{M}(\text{C22C}_2)]^+{}^d$	dimethylformamide	3.5^d	6.1^e	3.2^e		2.7^e	9.4^d

^a Errors represent one standard deviation. ^b This work. ^c Reference 10 and references therein. ^d Reference 13. ^e Reference 14.

Table II. Parameters for Metal (M^+) Ion Exchange on 1,4,7,10-Tetrakis(2-hydroxyethyl)-1,4,7,10-tetraazacyclododecane Complexes of Lithium(I) and Sodium(I)

[Li(thec12)] ⁺ in Methanol							
soln	$[M^+_{\text{solvated}}]$, mol dm ⁻³	$[[M(\text{thec12})]^+]$, mol dm ⁻³	$k_d(255.0 \text{ K})$, s ⁻¹	$k_d(298.2 \text{ K})$, s ⁻¹	ΔH_d^\ddagger , kJ mol ⁻¹	ΔS_d^\ddagger , J K ⁻¹ mol ⁻¹	
i	0.0360	0.0120	46.7 ± 1.4	746 ± 44	38.3 ± 1.0	-61.5 ± 3.7	
ii	0.0210	0.0270	47.3 ± 1.1	730 ± 28	37.8 ± 0.8	-63.3 ± 3.0	
iii	0.0187	0.0292	46.2 ± 0.7	712 ± 20	37.8 ± 0.5	-63.6 ± 1.8	
i-iii			46.7 ± 0.6	729 ± 17	38.0 ± 0.7	-62.8 ± 1.2	
[Li(thec12)] ⁺ in Dimethylformamide							
soln	$[M^+_{\text{solvated}}]$, mol dm ⁻³	$[[M(\text{thec12})]^+]$, mol dm ⁻³	$k_d(280.0 \text{ K})$, s ⁻¹	$k_d(298.2 \text{ K})$, s ⁻¹	ΔH_d^\ddagger , kJ mol ⁻¹	ΔS_d^\ddagger , J K ⁻¹ mol ⁻¹	
i	0.0354	0.0137	191 ± 6	621 ± 31	42.7 ± 1.8	-48.2 ± 6.4	
ii	0.0196	0.0295	185 ± 4	580 ± 35	41.4 ± 1.8	-53.2 ± 6.8	
iii	0.0088	0.0403	180 ± 5	561 ± 26	41.2 ± 1.2	-54.3 ± 4.4	
i-iii			185 ± 6	587 ± 31	41.8 ± 0.7	-51.9 ± 3.3	
[Na(thec12)] ⁺ in Methanol							
soln	$[M^+_{\text{solvated}}]$, mol dm ⁻³	$[[M(\text{thec12})]^+]$, mol dm ⁻³	$k_d(320.0 \text{ K})$, s ⁻¹	$k_d(298.2 \text{ K})$, s ⁻¹	ΔH_d^\ddagger , kJ mol ⁻¹	ΔS_d^\ddagger , J K ⁻¹ mol ⁻¹	
i	0.0412	0.0080	1478 ± 12	208 ± 3	68.6 ± 0.7	29.3 ± 2.2	
ii	0.0248	0.0248	1495 ± 44	212 ± 14	68.2 ± 2.6	28.1 ± 8.2	
iii	0.0109	0.0387	1445 ± 15	206 ± 4	68.1 ± 0.9	27.8 ± 2.8	
i-iii			1473 ± 25	209 ± 3	68.3 ± 1.4	28.4 ± 0.8	
[Na(thec12)] ⁺ in Dimethylformamide							
soln	$[M^+_{\text{solvated}}]$, mol dm ⁻³	$[[M(\text{thec12})]^+]$, mol dm ⁻³	$k_d(320.0 \text{ K})$, s ⁻¹	$k_d(298.2 \text{ K})$, s ⁻¹	ΔH_d^\ddagger , kJ mol ⁻¹	ΔS_d^\ddagger , J K ⁻¹ mol ⁻¹	
i	0.0395	0.0105	1506 ± 13	293 ± 4	56.9 ± 0.3	-6.9 ± 0.9	
ii	0.0250	0.0250	1527 ± 28	298 ± 9	56.8 ± 0.6	-7.2 ± 2.0	
iii	0.0115	0.0385	1521 ± 22	307 ± 7	55.5 ± 1.1	-11 ± 4	
i-iii			1518 ± 11	299 ± 7	56.4 ± 0.7	-8.4 ± 2.4	

Table III. Parameters for Lithium(I) and Sodium(I) Ion Exchange on 1,4,7,10-Tetrakis(2-hydroxyethyl)-1,4,7,10-tetraazacyclododecane Complexes and Other Complexes

complex	solvent	$10^{-5}k_c(298.2 \text{ K})$, dm ³ mol ⁻¹ s ⁻¹	$k_d(298.2 \text{ K})$, s ⁻¹	ΔH_d^\ddagger , kJ mol ⁻¹	ΔS_d^\ddagger , J K ⁻¹ mol ⁻¹
$[\text{Li}(\text{thec12})]^+{}^a$	methanol	8.97	729	38.0	-62.8
$[\text{Li}(\text{thec12})]^+{}^a$	dimethylformamide	5.74	587	41.8	-51.9
$[\text{Na}(\text{thec12})]^+{}^a$	methanol	70.8	209	68.3	28.4
$[\text{Na}(\text{thec12})]^+{}^a$	dimethylformamide	7.00	299	56.4	-8.4
$[\text{Li}(\text{C221})]^+{}^b$	methanol	192	78.4	23.8	-129
$[\text{Na}(\text{C221})]^+{}^c$	methanol	1700	0.0235		
$[\text{Na}(\text{C221})]^+{}^c$	dimethylformamide	180	0.25		
$[\text{Li}(\text{C22C}_2)]^+{}^d$	methanol	97.1	971	31.0	-84.0
$[\text{Li}(\text{C22C}_2)]^+{}^d$	dimethylformamide	7.60	240	22.5	-124
$[\text{Na}(\text{C22C}_2)]^+{}^e$	dimethylformamide	155	12.3	64.0	-9.5

^a This work. ^b Reference 11. ^c Reference 12. ^d Reference 13. ^e Reference 14.

Et₄NClO₄. An Orion Research SA 720 digital analyser was used to measure changes in potential for all titrations.

$$K = \frac{[[M(\text{thec12})]^+]}{[M^+][\text{thec12}]} \quad (1)$$

Results and Discussion

[M(thec12)]⁺ Stability. In methanol and dimethylformamide the apparent stability constant, K , of the alkali metal $[M(\text{thec12})]^+$ complexes varies in the sequence $\text{Li}^+ < \text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$, and K characterizing $[\text{Ag}(\text{thec12})]^+$ is much larger than that characterizing $[\text{Na}(\text{thec12})]^+$ (Table I). The selectivity of thec12 for Na^+ over Li^+ is not as high as that exhibited by the relatively rigid cryptand C221 and the clam-like C22C₂, and generally the K values for the alkali metal ion $[M(\text{thec12})]^+$ are lower (Table

I). This lower selectivity of thec12 is consistent with this flexible ligand more readily adapting to the size of the metal ion than is the case for C221, which has a preformed cavity of approximate radius³ of 1.10 Å, close to the optimum size for Na^+ ($r = 1.02$ Å),²⁹ while Li^+ and K^+ are, respectively, too small and too large to achieve an optimum fit. However, it was noted above that the number of thec12 hydroxo groups binding the metal ion is, respectively, one, three, and four in the case of Li^+ , Na^+ , and K^+ in the solid state,^{23,24} and it is anticipated that if a similar variation in solution exists it will have a substantial effect on the relative stabilities of the thec12 complexes. The selectivity of C22C₂ is

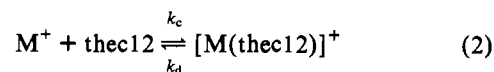
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based on the minimization of strain in $[M(C22C_2)]^+$ such that Na^+ forms the most stable complex as a consequence of the angle between the jaws of $[Na(C22C_2)]^+$ (89.6°) closely approaching the size of this angle in free $C22C_2$ (88.4°), while in $[Li(C22C_2)]^+$ and $[K(C22C_2)]^+$, respectively, the angle is too small and too large with the consequence that the resulting induced strain destabilizes these complexes by comparison with $[Na(C22C_2)]^+$.^{13,14} The lower overall stability of the alkali metal ion $[M(\text{thec12})]^+$ is probably a consequence of the flexible nature of thec12 also. The greater K values observed in methanol are consistent with this weaker electron donor solvent (Gutmann donor number $D_N = 23.5$)^{30,31} competing less effectively for metal ions than dimethylformamide ($D_N = 26.6$).³²

The stability of $[Ag(\text{thec12})]^+$ is greater than that of its alkali ion analogues as a consequence of the strong affinity of soft acid^{33,34} Ag^+ for the four nitrogens of the tetraaza macrocyclic ring.^{35,36} This affinity is such that the stability of $[Ag(\text{thec12})]^+$ is greater than that of $[Ag(C22C_2)]^+$ where only two nitrogens are available and approaches that of $[Ag(C221)]^+$ which also has only two nitrogens available but may have an enhanced stability as a consequence of Ag^+ ($r = 1.15 \text{ \AA}$)²⁹ approximating to the cavity size of C221.

$[M(\text{thec12})]^+$ Lability. Complete line shape analyses²⁷ of the temperature dependent coalescences of the 7Li and ^{23}Na resonances arising from the exchange of these nuclei between the solvated M^+ and $[M(\text{thec12})]^+$ environments (Figures 1 and 2) in methanol and dimethylformamide yield τ_c , the mean lifetime of M^+ in $[M(\text{thec12})]^+$, for the solutions whose compositions are given in Table II. (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 $[M(\text{thec12})]^+$ and solvent are very similar (Figure 3). This indicates that the mean lifetime of $[M(\text{thec12})]^+$, $\tau_c = 1/k_d$, (where k_d is the decomplexation rate constant) is independent of the concentration of solvated M^+ (Table II) consistent with the

nonparticipation of solvated M^+ in the rate-determining step of the dominant pathway for M^+ exchange on $[M(\text{thec12})]^+$. This is compatible with the operation of a monomolecular mechanism for the decomplexation of M^+ from $[M(\text{thec12})]^+$ as shown in eq 2 where $k_c (=k_dK)$ is the complexation rate constant. The kinetic parameters for the decomplexation of $[M(\text{thec12})]^+$ (Table II) are derived from the temperature variation of τ_c through eq 3 where all symbols have their usual meanings.



$$k_d = 1/\tau_c = (k_B T/h) \exp(-\Delta H_d^*/RT + \Delta S_d^*/R) \quad (3)$$

The smaller ΔH_d^* (despite the more negative ΔS_d^*) characterizing $[Li(\text{thec12})]^+$ renders it more labile toward decomplexation than $[Na(\text{thec12})]^+$ in methanol and dimethylformamide, and the consequently smaller k_d characterizing $[Na(\text{thec12})]^+$ contributes to its greater stability by comparison with $[Li(\text{thec12})]^+$. (The significant differences in ΔH_d^* and ΔS_d^* characterizing the two systems may indicate mechanistic differences between them arising from different numbers of thec12 hydroxo groups binding Li^+ and Na^+ , but this study does not reveal the details of the sequential decomplexation and complexation mechanisms.) This difference in lability is small by comparison with the 3000-fold difference in k_d characterizing $[Li(C221)]^+$ and $[Na(C221)]^+$ in methanol (Table III), which demonstrates the more incisive influence of the rigid preformed cavity of C221 on selectivity in its complexes and which largely accounts for the much greater stability of the latter complex. In dimethylformamide, k_d characterizing $[Li(C22C_2)]^+$ is $\sim 20k_d$ characterizing $[Na(C22C_2)]^+$, which together with the ~ 20 -fold greater k_c of the latter species accounts for its greater stability by comparison with $[Li(C22C_2)]^+$. These variations in k_d and k_c are consistent with flexible thec12 adapting more readily to the size requirements of Li^+ and Na^+ , and consequently being less selective in complexing these ions than is the case with less flexible C221 and C22C₂.

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