and is a reaction possibility long recognized.

The slow rate of reaction of O_2 with V(II) in CH_3CN is not unexpected in view of the high oxidation potential (1.25 V). That the reaction takes place at a noticeable rate suggests strongly that oxidation by O_2 is assisted by bond formation as suggested above. Quite unexpected is the slow rate of reaction of V(II) in CH_3OH as compared to that in H_2O. A contributing factor may well be steric demands of the methyl groups, which would interfere with bond formation through the faces of the octahedron. Equally unexpected is the observation that in neither CH_3CN or CH_3OH does $[VOV]^{4+}$ appear as an intermediate product in a recognizable amount.

The dominant product of the reaction of epoxides and of O_2 with V(II) in CH_2Cl_2 or DME as solvent is $[VOV]^{4+}$. To learn whether this species is the immediate product of the reaction of O_2 with V(II) or whether V(IV) is the immediate product, which then reacts with V(II) to form $[VOV]^{4+}$, two kinds of experiments were performed. In one approach, the order of mixing for the most reactive epoxide, namely that derived from styrene, was reversed. The usual procedure was to add the epoxide to a solution of V(II), an arrangement that favors the reaction of V(IV) as a primary product with V(II). Reversing the order of mixing did not lead to a substantial reduction in the yield of the binuclear ion. The experiment however must be regarded as inconclusive because we cannot be sure that the reaction of V(II) with epoxide is rapid enough to make this simple strategy effective. In the second approach, efforts were made to measure the rate of reaction of V(II) with V(IV), the latter prepared by the reaction of V(II) with O_2. Reaction was continued, passing O_2 until the color of $[VOV]^{4+}$, which is the product first formed, was depleted—this leaves a solution that is a clear blue, characteristic of VO^{2+}—or in some cases, some residual $[VOV]^{4+}$ was left. The interaction of V(II) with VO^{2+} thus prepared is slow enough so that we could be certain that in the case of the more reactive epoxides, $[VOV]^{4+}$ is indeed a direct product of the reaction, were it not for the fact that unexpected complications were encountered in the studies.

One of these complications was namely that when clear blue solutions of VO^{2+} were used, in some cases a considerable amount of V(II) was consumed before the color characteristic of $[VOV]^{4+}$ appeared. This effect can be attributed to the presence of some V(V) in such solutions, as is indicated also by experiments in which I^- is used as reducing agent. More difficult to understand is the observation that as the V(II) is increased in proportion to VO^{2+} kept in excess, the concentration of $[VOV]^{4+}$, making due allowance for the effect of dilution, does not increase linearly. Rather a saturation effect is observed, as would be expected for a system in which there is a measurable equilibrium between reactants and products, so that the end points is obscured. Reasonable conjectures are that V(II) and VO^{2+}, or mononuclear V(III), are in equilibrium with $[VOV]^{4+}$, but as described elsewhere,[16] the effects expected on dilution, if a simple equlibrium such as

$$VO^{2+} + V(II) = [VOV]^{4+}$$

were involved, are not observed. Finally, measurements of the rate of reaction show complex kinetics. In experiments with V(II) in excess, the rate is almost independent of the concentration of V(II) (over the range 10^{-5}–10^{-2} M) while when V(IV) is in excess, the reaction shows an induction period.

We conclude that we cannot be certain of the physical state of either $[VOV]^{4+}$ or VO^{2+} in these solutions, and one or both may be polynuclear. As a result, we can reach no conclusion on the issue that motivated us to undertake these experiments, because there is a real possibility that V(IV), as first produced, is different from V(IV) as it is present in the aged solutions we have dealt with in the experiments just mentioned, which we have not reported in detail.

It needs to be acknowledged that the composition of the first sphere of coordination of V(II) in the solvents acetonitrile, pyridine, and acetone with triflate as the counter ion is not known. These solvents, being non-protic, do not greatly stabilize the free anion, and thus, while we have tacitly assumed that in acetonitrile, for example, the cation exists as $V(CH_3CN)_6^{2+}$, the anions may in fact be ligated to the metal ion. This issue is now under investigation.

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Complexation of Lithium(I) and Silver(I) by 4,7,13,16-Tetraoxa-1,10-diazabicyclo[8.8.2]eicosane in a Range of Solvents. A ^{7}Li Nuclear Magnetic Resonance and Potentiometric Titration Study

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Complexation of Li^+ and Ag^+ by the clamlike cryptand 4,7,13,16-tetraoxa-1,10-diazabicyclo[8.8.2]eicosane ($C22C_2$) to form the cryptate $[Li.C22C_2]^+$ has been studied in seven solvents by ^{7}Li NMR spectroscopy and potentiometric titration. A considerable variation in the $[Li.C22C_2]^+$ and $[Ag.C22C_2]^+$ stability constants (shown as the respective log (K/dm^3 mol^{-1}) values at 298.2 K after each solvent) occurs with solvent variation: acetonitrile (7.8, 9.4), acetone (8.9, 13.1), water (<2, 6.0), methanol (4.0, 10.2), dimethylformamide (3.5, 9.4), diethylformamide (3.1, 8.2), and pyridine (4.0, 5.0). The exchange of Li^+ on $[Li.C22C_2]^+$ falls within the ^{7}Li NMR time scale in methanol, dimethylformamide, and diethylformamide, in which the monomolecular decomplexation process is characterized by $k_d(298.2\ K) = 971 \pm 42$, 240 ± 7, and $916 \pm 28\ s^{-1}$, respectively, $\Delta H_d^* = 31.0 \pm 0.4$, 22.5 ± 1.3, and 26.7 ± 0.6 kJ mol^{-1}, respectively, and $\Delta S_d^* = -83.9 \pm 1.8$, -124 ± 5, and -99 ± 2 J K^{-1} mol^{-1}, respectively. In acetonitrile, acetone, and pyridine the exchange rate is in the very slow regime of the ^{7}Li NMR time scale close to the solvent boiling point and in the very fast regime in water close to the freezing point. These data are discussed in the context of the effects of cryptand structure and solvent characteristics on cryptate lability and stability.

Introduction

Complexation of alkali-metal ions by (polyoxa)diazabicycloalkanes, or cryptands, to form cryptates has generated substantial interest since Lehn first reported the cryptands.[1-19] We have been particularly interested in the relationship between cryptate structure, stability, and lability and herein report a kinetic

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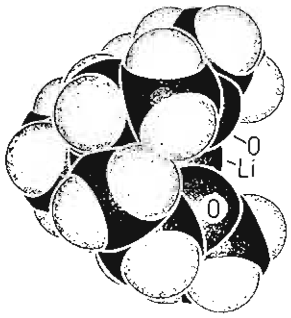
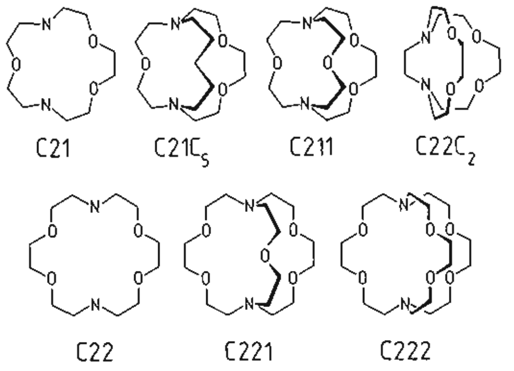


Figure 1. Structure of $[Li.C22C_2]^+$ viewed almost perpendicular to the N–N axis. The atomic coordinates are taken from the crystal structure[19] and all atoms are shown as spheres of appropriate radii. The structural diagram was generated by using the program SCHAKAL.[20]

Chart I. Diaza Crown Ethers and Cryptand Structures



and equilibrium study of $[Li.C22C_2]^+$, (4,7,13,16-tetraoxa-1,10-diazabicyclo[8.8.2]eicosane)lithium(I),[18,19] and its Ag^+ analogue in a range of solvents, which affords a systematic comparison with the complexation of Li^+ and Ag^+ by related cryptands and diaza crown ethers shown in Chart I. The cryptand $C22C_2$ has an unusual clamlike structure resulting from the shortness of the C_2 arm, as is shown in the space-filling representation of $[Li.C22C_2]^+$ (Figure 1) generated from X-ray diffraction data.[19,20] It is seen that Li^+ in $[Li.C22C_2]^+$ is sited deep in the throat of the cryptand, which contrasts with the solid-state structures of $[Li.C21C_5]^+$ and $[Li.C211]^+$ in which Li^+ is centrally sited in the approximately spherical cavities of the cryptands.[15,16] An additional feature of $C22C_2$ is that its bicyclic structure contains one arm that possesses no donor atoms, as does the structure of $C21C_5$. Thus $C21C_5$ and $C22C_2$ represent intermediate structural stages between the diaza crown ethers C21 and C22 and the cryptands C211, C221, and C222, in which all three arms possess donor atoms. The effects of these differences on the stability and lability of $[Li.C22C_2]^+$ and $[Ag.C22C_2]^+$ in a range of solvents are examined in this study.

Experimental Section

The cryptand $C22C_2$ was prepared as described previously.[18] Lithium perchlorate (Fluka) was vacuum-dried at 353–363 K for 48 h and was then stored over P_2O_5 under vacuum. Water was triply distilled. Acetonitrile, methanol, dimethylformamide, pyridine, dimethyl sulfoxide, and propylene carbonate were purified and dried by literature methods[21] and were stored under nitrogen over Linde 3A molecular sieves in the cases of methanol and acetonitrile and over Linde 4A molecular sieves for the other solvents. The water content of these solvents was below the Karl Fischer detection level of approximately 50 ppm. Solutions of $LiClO_4$ and $C22C_2$ were prepared under dry nitrogen in a glovebox. For ^7Li NMR studies these solutions were degassed and sealed under vacuum in 5-mm NMR tubes that 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 NMR spectra were run at 116.59 MHz on a Bruker CXP-300 spectrometer. An average of 1000 transients were accumulated in a 2048 data base over a 8000-Hz spectral width for each solution prior to Fourier transformation. The solution temperature was controlled to within ±0.3 K by using a Bruker B-VT 1000 temperature controller. The Fourier-transformed spectra were subjected to complete line shape analysis[22] on a VAX 11-780 system to obtain kinetic data. The temperature-dependent ^7Li line widths and chemical shifts employed in the line shape analysis were extrapolated from low temperatures where no exchange-induced modification occurred.

Stability constants for $[Ag.C22C_2]^+$ were determined through duplicate potentiometric titrations of 25 cm^3 of 10^{-3} mol dm^{-3} $AgClO_4$ solution with 10^{-2} mol dm^{-3} $C22C_2$ solution. These data were employed in the derivation of the stability constants of $[Li.C22C_2]^+$ from data obtained from a competitive potentiometric titration of 25 cm^3 of 10^{-3} mol dm^{-3} $AgClO_4$ solution with a solution 10^{-2} mol dm^{-3} in both $LiClO_4$ and $C22C_2$, as described in the literature.[8] The titrations were carried out under dry nitrogen in a thermostated (298.2 ± 0.01 K) titration vessel connected to a thermostated reference vessel by a salt bridge. The reference and titration electrodes were silver, and the reference solution was 10^{-2} mol dm^{-3} $AgClO_4$ in the solvent under investigation. For a given titration the titration and reference vessels and the salt bridge contained solutions made up in the same solvent, and all solutions, including that titrated into the titration vessel, were 0.05 mol dm^{-3} in Et_4NClO_4. An Orion Research SA 720 digital analyzer was used to measure changes in potential.

Results and Discussion

Cryptate Stability. The complexation of Li(I) and Ag(I) by $C22C_2$ was studied in seven solvents (Table I) selected to provide a range of electron-donating abilities, as indicated by their Gutmann donor numbers (D_N),[23-25] and also to provide a contrast between the effects of oxygen and nitrogen donor solvents. It is seen that in these solvents the stability of $[Li.C22C_2]^+$ is substantially less than that of $[Ag.C22C_2]^+$ and that the difference in stability is less in the nitrogen donor solvents acetonitrile and pyridine. This is consistent with a combination of the tendency for nondirectional-bonding Li^+ to show a preference for oxygen donor atoms and that of directional-bonding Ag^+ (which has a tendency to form two strong coaxial bonds) to show a preference for nitrogen donor atoms.[26,27] Thus the smaller difference in stability in the nitrogen donor solvents reflects the tendency of Ag^+ to bond less effectively with oxygen donor atoms than with nitrogen donor atoms, with the consequence that a nitrogen donor

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Table I. Stability Constants[a] for the Complexation of Li^+ and Ag^+ by 4,7,13,16-Tetraoxa-1,10-diazabicyclo[8.8.2]eicosane ($C22C_2$) and Other Cryptands and Diaza Crown Ethers at 298.2 K

		log (K/dm^3 mol^{-1})						
solvent	D_N[b]	$[Li.C22C_2]^{+c}$	$[Li.C21C_5]^{+d}$	$[Li.C211]^{+e}$	$[Li.C221]^{+e}$	$[Li.C222]^{+e}$	$[Li.C21]^+$	$[Li.C22]^{+f}$
acetonitrile	14.1	7.8 ± 0.1	4.15	>10	10.33	6.97		4.39
acetone	17.0	8.9 ± 0.1						2.13
water	18.0 (33.0)[g]	<2		5.5	2.50	0.98		
methanol	19.0 (23.5)[g]	4.0 ± 0.1	3.01	8.04	5.38	2.6		
dimethylformamide	26.6	3.5 ± 0.1	1.80	6.99	3.58			~0.0
diethylformamide	30.9	3.1 ± 0.1						
pyridine	33.1	4.0 ± 0.1						0.43

		log (K/dm^3 mol^{-1})						
solvent	D_N[b]	$[Ag.C22C_2]^{+c}$	$[Ag.C21C_5]^{+d}$	$[Ag.C211]^{+e}$	$[Ag.C221]^{+e}$	$[Ag.C222]^{+e}$	$[Ag.C21]^+$	$[Ag.C22]^+$
acetonitrile	14.1	9.4 ± 0.1	4.29	7.70	11.24	8.99		
acetone	17.0	13.1 ± 0.1						
water	18.0 (33.0)[g]	6.0 ± 0.1		8.5	10.6	9.6		7.90[h]
methanol	19.0 (23.5)[g]	10.2 ± 0.1	7.69	10.60	14.64	12.20	7.63[i]	10.02[i]
dimethylformamide	26.6	9.4 ± 0.1	5.23	8.60	12.41	10.07		
diethylformamide	30.9	8.2 ± 0.1						
pyridine	33.1	5.0 ± 0.1						

[a] In 0.05 mol dm^{-3} Et_4NClO_4 supporting electrolyte unless otherwise indicated. [b] Gutmann donor number from ref 23. [c] This work. [d] Reference 17. [e] Reference 9 and references therein. [f] Shamsipur, M.; Popov, A. I. *Inorg. Chim. Acta* **1980**, *43*, 243–247. In this study I = 0.0025 mol dm^{-3} ($LiClO_4$). [g] In refs 24 and 25 it has been suggested that D_N = 33.0 and 23.5 are more appropriate in water and methanol solutions than D_N = 18.0 and 19.0, respectively, obtained in 1,2-dichloroethane solution where the hydrogen-bonding structure of water and methanol is disrupted. [h] Arnaud-Neu, F.; Spiess, B.; Schwing-Weill, M. J. *Helv. Chim. Acta* **1977**, *60*, 2633–2643. In 0.1 mol dm^{-3} Et_4NClO_4 supporting electrolyte. [i] Reference 27.

solvent can compete more strongly with a cryptand for Ag^+ than can an oxygen donor solvent. This is also reflected in the variation of stability with the nature of the solvent. Thus for $[Li.C22C_2]^+$ stability tends to decrease as D_N increases. The apparently anomalous position of water in the sequence is resolved when a D_N value = 33.0 is employed, which is probably more appropriate to aqueous solutions than D_N = 18.0.[24,25] On this basis the stability of $[Li.C22C_2]^+$ is higher than expected in pyridine, for which D_N = 33.1, and may indicate that the incorporation of the nitrogen donor atom in the ring structure causes steric hindrance which decreases the solvating power of pyridine. While the stability sequence for $[Ag.C22C_2]^+$ in the oxygen donor solvents is similar to that for $[Li.C22C_2]^+$, the stability of $[Ag.C22C_2]^+$ is decreased in acetonitrile and pyridine as a consequence of the greater ability of these nitrogen donor solvents to compete with $C22C_2$ for Ag^+.

Generally, stabilities increase in the sequence $[Li.C21C_5]^+ \sim [Li.C22]^+ < [Li.C222]^+ < [Li.C22C_2]^+ < [Li.C221]^+ < [Li.C211]^+$, consistent with the six donor atoms of C211 and the optimal fit of Li^+ (r = 76 pm)[28] into the C211 cavity (r ~ 80 pm)[1] in *inclusive* $[Li.C211]^+$, generating the greatest stability. The increase in stability $[Li.C222]^+ < [Li.C221]^+$ indicates that the effect of the decrease in electrostatic interaction with Li^+ resulting from the decrease in the number of donor atoms from 8 in C222 to 7 in C221 is offset by the smaller cavity size of C221, with the consequence that $[Li.C221]^+$ is the more stable cryptate. Similarly, the increase in stability $[Li.C22]^+ < [Li.C22C_2]^+ < [Li.C211]^+$ indicates the influence of ligand stereochemistry on ligands with the same number and type of donor atoms whereby the flexible partial cavity formed when monocyclic C22 binds Li^+ confers less stability than the preformed cavities of the two cryptands.

The number of donor atoms is more influential in determining the relative stabilities of the Ag^+ species as exemplified by the sequence $[Ag.C21]^+ \sim [Ag.C21C_5] < [Ag.C22]^+ \sim [Ag.C211]^+ \sim [Ag.C22C_2]^+ < [Ag.C222]^+ < [Ag.C221]^+$ in methanol. (The sequence $[Ag.C222]^+ < [Ag.C221]^+$ may indicate the superimposition of steric effects as Ag^+ (r=115 pm)[28] fits the C221 cavity (r ~ 110 ppm)[1] optimally while it fits the C222 cavity (r ~ 140 pm) loosely, and in consequence, $[Ag.C221]^+$ should gain an enhancement of stability over $[Ag.C222]^+$.) The stabilities of the Ag^+ complexes decrease in acetonitrile, both in absolute magnitude and relative to the analogous Li^+ complexes, as a consequence of the ability of this nitrogen donor solvent to compete with ligands for Ag^+ to a greater extent than do oxygen donor solvents. In the common oxygen donor solvents studied, methanol and dimethylformamide, the Li^+ cryptates are less stable than their Ag^+ analogues, but the difference in stability is less for $[M.C211]^+$. This probably reflects the increased stability characterizing $[Li.C211]^+$ because of its *inclusive* structure, whereas the larger Ag^+ is unlikely to form an inclusive cryptate with C211 and gain this enhanced stability. A combination of the inclusive nature of $[Li.C211]^+$ and the greater ability of a nitrogen donor solvent to compete for Ag^+ accounts for the reversal of stability to $[Li.C211]^+ > [Ag.C211]^+$ found in acetonitrile.

Generally, it appears that variation in the character of the cryptands, diaza crown ethers, metal ions, and solvent interactions with the free and complexed metal ions are dominant factors determining the variations in stability of cryptates and diaza crown ether complexes. However, there is evidence that direct interactions between some solvents and cryptands[29] and crown ethers[30] can occur, and it may be that the solvational changes of the cryptands and diaza crown ethers and solvent influence on conformational changes occurring in the complexation processes also contribute to the variation of stability with the nature of the solvent, but such contributions are not readily identified in this study.

Cryptate Lability. In methanol, dimethylformamide, and diethylformamide complete line shape analysis[22] of the temperature-dependent coalescence of the ^7Li resonances arising from solvated Li^+ and $[Li.C22C_2]^+$ (Figure 2) yields τ_c, the mean lifetime of Li^+ in $[Li.C22C_2]^+$, for 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 Li^+ in the fully solvated state and X_c and X_s are the corresponding mole fractions.) 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 $[Li.C22C2]^+$, τ_c ($=1/k_d$, where k_d is the decomplexation rate constant), is independent of the concentration of solvated Li^+ (Table II), consistent with the nonparticipation of solvated Li^+ in the rate-determining step of the predominant pathway for Li^+ exchange on $[Li.C22C2]^+$, and the operation of a monomolecular mechanism for the decomplexation of Li^+ from

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Table II. Lithium Ion Exchange on $[Li.C22C_2]^+$ in Methanol, Dimethylformamide, and Diethylformamide and Solution Composition and Kinetic Parameters[a]

soln	solvent	$[Li^+_{solv}]$, mol dm^{-3}	$[Li.C22C_2^+]$, mol dm^{-3}	k_d(240.0 K), s^{-1}	k_d(298.2 K), s^{-1}	ΔH_d^*, kJ mol^{-1}	ΔS_d^*, J K^{-1} mol^{-1}
i	methanol	0.01001	0.0093	37.7 ± 0.6	972 ± 40	31.0 ± 0.4	−84.0 ± 2.6
ii		0.0073	0.0113	37.4 ± 0.3	860 ± 42	29.9 ± 0.5	−88.7 ± 3.1
iii		0.0128	0.0075	37.9 ± 0.4	1022 ± 61	31.7 ± 0.4	−81.1 ± 1.6
i–iii				37.9 ± 0.4	971 ± 42	31.0 ± 0.4	−83.9 ± 1.8
i	dimethylformamide	0.0117	0.0112		235 ± 7	21.9 ± 1.5	−126 ± 5
ii		0.0071	0.0132		246 ± 9	22.5 ± 1.2	−124 ± 4
iii		0.0143	0.0060		240 ± 7	23.1 ± 1.5	−120 ± 5
i–iii					240 ± 7	22.5 ± 1.3	−124 ± 5
i	diethylformamide	0.0138	0.0068	216 ± 4[b]	938 ± 20	26.7 ± 0.6	−98 ± 2
ii		0.0113	0.0093	232 ± 9	913 ± 62	24.8 ± 1.3	−105 ± 5
iii		0.0070	0.0136	202 ± 2	879 ± 22	26.8 ± 0.4	−99 ± 2
i–iii				216 ± 4	916 ± 28	26.7 ± 0.6	−99 ± 2

[a] Errors represent one standard deviation from the least-squares fit of the experimental τ_c data to eq 2. [b] At 265.0 K.

Table III. Kinetic Parameters for Li^+ Exchange on $[Li.C22C_2]^+$ and Other Cryptates in a Range of Solvents

solvent	D_N[a]	$10^{-5}k_c$(298.2 K),[b] dm^3 mol^{-1} s^{-1}	k_d(298.2 K), s^{-1}	ΔH_d^*, kJ mol^{-1}	ΔS_d^*, J K^{-1} mol^{-1}
		$[Li.C22C_2]^+$[c]			
acetonitrile	14.1		<10		
methanol	19.0 (23.5)[d]	97.1	971 ± 42	31.0 ± 0.4	−84.0 ± 2.6
dimethylformamide	26.6	7.60	240 ± 7	22.5 ± 1.2	−124 ± 5
diethylformamide	30.9	11.5	916 ± 28	26.7 ± 0.6	−98.6 ± 2.3
		$[Li.C21C_5]^+$[e]			
methanol	19.0 (23.5)[d]	0.221	21.6	36.1	−98.4
dimethylformamide	26.6	0.073	116	38.4	−76.5
diethylformamide	30.9	0.149	210	27.8	−108
		$[Li.C211]^+$			
methanol	19.0 (23.5)[d]	4.8[f]	4.4×10^{-3}		
dimethylformamide	26.6	1.27[g]	0.0130	64.4	−64.8
		$[Li.C221]^+$[h]			
methanol	19.0 (23.5)[d]	192	78.4	23.8	−129
		$[Li.C222]^+$			
acetonitrile	14.1	39200	420[h]	11.6	−157
methanol	19.0 (23.5)[d]		>300[f]		

[a] Gutmann donor numbers from ref 23. [b] $k_c = K/k_d$ where K values appear in Table I. [c] This work. The errors represent one standard deviation obtained from a linear regression analysis of the temperature dependence of experimental τ_c data through eq 2. The exchange mechanism in acetonitrile is not known, and thus the limiting value of k_d ($=1/\tau_c$) in acetonitrile provides a simple comparison with k_d characterizing $[Li.C222]^+$, which exchanges through a monomolecular mechanism. [d] This alternative D_N value has been suggested in ref 25. [e] Data from ref 17. [f] Data from ref 8. [g] Data from ref 5. [h] Data from ref 7.

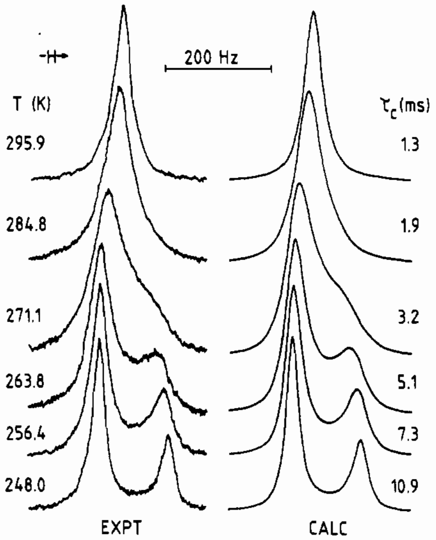

Figure 2. Typical exchange-modified 116.59-MHz ^7Li NMR spectra of a diethylformamide solution of $LiClO_4$ (0.0206 mol dm^{-3}) and $C22C_2$ (0.0068 mol dm^{-3}). Experimental temperatures and spectra appear to the left of the figure, and the best fit calculated line shapes and corresponding τ_c values appear to the right. The resonance of $[Li.C22C_2]^+$ appears upfield from that of solvated Li^+.

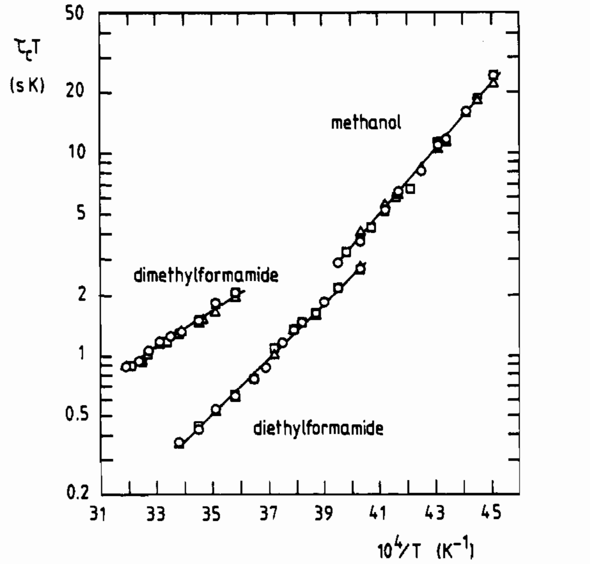

Figure 3. The temperature variation of τ_c for Li^+ exchange on $[Li.C22C_2]^+$ in methanol, dimethylformamide, and diethylformamide. For each solvent, data points for solutions i–iii are represented by circles, triangles, and squares, respectively. The solid lines represent the best fits of the combined data for each trio of solutions to eq 2.

the cryptand, as shown in eq 1, in which k_c is the complexation rate constant. The kinetic parameters for the decomplexation

$$\mathrm{Li^+ + C22C_2 \underset{k_d}{\overset{k_c}{\rightleftharpoons}} [Li.C22C_2]^+} \qquad (1)$$

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

of $[\mathrm{Li.C22C_2}]^+$ (Table II) are derived from the temperature variation of τ_c through eq 2, in which all symbols have their usual meaning.

In acetonitrile, acetone, and pyridine the rate of exchange of $\mathrm{Li^+}$ between the solvated and $[\mathrm{Li.C22C_2}]^+$ environments is too slow to cause any significant broadening of the separate $^7\mathrm{Li}$ resonances characterizing these environments close to the solvent boiling point temperature. However, a conservative lower limit for $\tau_c(298.2\ \mathrm{K}) \sim 100$ ms may be estimated in acetonitrile, acetone, and pyridine, respectively, by calculating a τ_c that would broaden the $[\mathrm{Li.C22C_2}]^+$ observed resonance width by a factor of 1.5. In water a single narrow resonance is observed for solutions containing $[\mathrm{Li.C22C_2}]^+$ and solvated $\mathrm{Li^+}$ at temperatures close to the freezing point, consistent with exchange being in the very fast limit of the NMR time scale. This variation in lability with the nature of the solvent is similar to that observed for other cryptates, for which it is generally found that the magnitude of k_d increases with solvent D_N and is much more dependent on the nature of the solvent than is that of k_c, consistent with the transition state being more similar to the solvated metal ion and the free cryptand than to the cryptate.[9,14,17]

The $[\mathrm{Li.C22C_2}]^+$ data may be compared with those characterizing $[\mathrm{Li.C21C_5}]^+$, $[\mathrm{Li.C211}]^+$, $[\mathrm{Li.C221}]^+$, and $[\mathrm{Li.C222}]^+$, for which monomolecular decomplexation mechanisms also operate in the solvents listed in Table III.[5,7,17] (Sometimes a bimolecular exchange mechanism operates as observed for $[\mathrm{Li.C221}]^+$ in acetonitrile and propylene carbonate, consistent with solvents of higher dielectric constants favoring a bimolecular transition state for some cryptates.[7]) The more open and flexible structure of $\mathrm{C22C_2}$ probably accounts for the greater k_c and k_d values characterizing $[\mathrm{Li.C22C_2}]^+$ by comparison with those of the relatively rigid *inclusive* $[\mathrm{Li.C211}]^+$, in which $\mathrm{Li^+}$ is bound by the same number and type of donor atoms. Although $\mathrm{C21C_5}$ has one less donor than $\mathrm{C22C_2}$, its relative rigidity also confers a lower lability on $[\mathrm{Li.C21C_5}]^+$ (which exists in an *exclusive–inclusive* equilibrium in solution)[17] than $\mathrm{C22C_2}$ does on $[\mathrm{Li.C22C_2}]^+$. As size increases, cryptand flexibility also increases and the optimum fit of $\mathrm{Li^+}$ to the cryptand cavity is lost with the consequence that the labilities of $[\mathrm{Li.C221}]^+$ and $[\mathrm{Li.C222}]^+$ approach that of $[\mathrm{Li.C22C_2}]^+$.

Conclusion

The open and flexible structure of $\mathrm{C22C_2}$ results in $[\mathrm{Li.C22C_2}]^+$ being less stable and more labile than *inclusive* $[\mathrm{Li.C211}]^+$, which has the same number and type of donor atoms but which has a more rigid structure. However, as a consequence of its clamlike structure, $\mathrm{C22C_2}$ is more able to approach optimum bonding distances with $\mathrm{Li^+}$ than is C222, despite the latter cryptand possessing more donor atoms, with the consequence that $[\mathrm{Li.C22C_2}]^+$ is more stable and of a similar or lesser lability than $[\mathrm{Li.C222}]^+$, depending on the solvent. These comparisons illustrate the interplay of the effects of the number of donor atoms and cryptand flexibility which produce variations in cryptate stability and lability. A major factor producing the greater stability of $[\mathrm{Ag.C22C_2}]^+$, by comparison with that of $[\mathrm{Li.C22C_2}]^+$, is the greater ability of $\mathrm{Ag^+}$ to bind to nitrogen donor atoms. This also explains the decrease in this stability difference observed in acetonitrile for this and other cryptate pairs that occurs as a consequence of the ability of acetonitrile to solvate $\mathrm{Ag^+}$ more strongly, by comparison to oxygen donor solvents, than is the case for $\mathrm{Li^+}$.

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Importance of Ion Association in the Induced Reactions of Cobalt(III)–Acido Complexes. 7. The $\mathrm{Hg^{2+}}$-Assisted Reaction of *t*-$[\mathrm{Co(tren)(NH_3)X}]^{2+}$ ($\mathrm{X = Cl^-, Br^-}$) in Aqueous Solution

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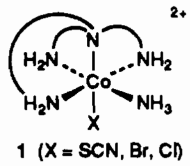
The $\mathrm{Hg^{2+}}$-promoted reaction of *t*-$[\mathrm{Co(tren)(NH_3)X}]^{2+}$ ions (hereafter *t*-$\mathrm{CoX^{2+}}$, X = Br, Cl) in NaY electrolytes of varying type ($\mathrm{Y = NO_3^-, ClO_4^-, CF_3SO_3^-}$) and concentration ($[\mathrm{Y^-}] = 0$-$1.0$ M; $[\mathrm{NO_3^-}] + [\mathrm{Y^-}] = 1.0$ M) follows the rate law $k_{obs} = (k_0K_0 + k_YK_YK_{Hg}[\mathrm{Y^-}])[\mathrm{Hg}]_T/(1 + K_{Hg}[\mathrm{Y^-}] + (K_0 + K_Y)[\mathrm{Hg}]_T)$, in which k_0 and k_Y represent first-order rate constants for aquation and anation of the associated species *t*-$\mathrm{CoXHg^{4+}}$ and *t*-$\mathrm{CoXHgY^{3+}}$, respectively. Reaction products are correlated by using the same expression with *t*-$\mathrm{CoXHg^{4+}}$ forming only $\mathrm{CoOH_2^{3+}}$ and *t*-$\mathrm{CoXHgY^{3+}}$ forming both $\mathrm{CoOH_2^{3+}}$ and $\mathrm{CoY^{2+}}$ products (57% $\mathrm{CoONO_2^{2+}}$ for X = Br, Cl; ~20% $\mathrm{CoOSO_2CF_3^{2+}}$ for X = Br). Both the rate and products are almost independent of the type and concentration of electrolyte cation ($\mathrm{Na^+, K^+, Ba^{2+}, Sr^{2+}, Mg^{2+}, La^{3+}}$). Comparison is made with the analogous *t*-$\mathrm{CoSCN^{2+}} + \mathrm{Hg^{2+}}$ reaction (in which $\mathrm{CoNCS^{2+}}$ is an additional product[1]), and it is suggested that products are decided by associations occurring before breaking of the Co–X bond with little or no discrimination between entering groups. Rate data for the spontaneous hydrolysis of *t*-$\mathrm{CoX^{2+}}$ species ($\mathrm{X = Cl, Br, CF_3SO_3, NO_3}$) are given.

Introduction

In a previous article,[1] we showed that the $\mathrm{Hg^{2+}}$-assisted reaction of *t*-$[\mathrm{Co(tren)(NH_3)SCN}]^{2+}$ (hereafter designated $\mathrm{CoSCN^{2+}}$ (**1**)) results in both the entry of solvent giving $\mathrm{CoOH_2^{3+}}$ and the isomerization of coordinated thiocyanate giving $\mathrm{CoNCS^{2+}}$ (eq 1). Previous to our investigation, Adegite, Orhanovic, and Sutin[2] had



1 (X = SCN, Br, Cl)

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(1) Buckingham, D. A.; Clark, C. R.; Gaudin, M. J. *Inorg. Chem.* **1988**, *27*, 293.

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