mining the origin of the effect of the cyclohexylene bridge on metal ion size based selectivity. It may be that the effect derives, not so much from the presence of the cyclohexylene bridge in a particular chelate ring, as from the effect of the increased rigidity of this chelate ring on the ability of the remaining donor groups of the ligand to be oriented for coordination to metal ions of differing sizes. This study has indicated that the cyclohexylene bridge could be a useful tool in altering the selectivities of ligands in favor of smaller metal ions and also in the synthesis of more powerfully complexing ligands.

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Complexation of Sodium(I) and Other Monovalent Ions by 4,7,13,16-Tetraoxa-1,10-diazabicyclo[8.8.2]eicosane in a Range of Solvents. A Potentiometric Titration and ^{23}Na Nuclear Magnetic Resonance Study

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Complexation of Li^+, Na^+, K^+, Cs^+, Ag^+, and Tl^+ by the clamlike cryptand 4,7,13,16-tetraoxa-1,10-diazabicyclo[8.8.2]eicosane ($C22C_2$) to form the cryptate $[M.C22C_2]^+$ has been studied in six solvents by potentiometric titration and ^{23}Na NMR spectroscopy. A considerable variation in the stability of $[M.C22C_2]^+$ occurs as M^+ is varied in the sequence Li^+ (3.5), Na^+ (6.1), K^+ (3.2), Cs^+ (2.7), Ag^+ (9.4), and Tl^+ (6.7), where the figures in parentheses are log (K/dm^3 mol^{-1}) and K is the apparent stability constant of $[M.C22C_2]^+$ in dimethylformamide at 298.2 K. Crystallographic data show that the dihedral angle between the jaws of $C22C_2$ in the free cryptand, $[Li.C22C_2]^+$, $[Na.C22C_2]^+$, and $[K.C22C_2]^+$ is 88.4, 70.9, 89.6, and 100°, respectively. These two data sets indicate that a dominant factor controlling the stability of the alkali-metal cryptates is the increase in strain energy associated with the deviation of the $C22C_2$ jaw angle in $[M.C22C_2]^+$ from that in free $C22C_2$, with the consequence that $[Na.C22C_2]^+$ is the most stable cryptate. The relative magnitudes of K are similar in other solvents, but the absolute magnitude exhibits substantial variation as the nature of the solvent changes. The exchange of Na^+ on $[Na.C22C_2]^+$ falls within the ^{23}Na NMR time scale in water, dimethylformamide, and dimethyl sulfoxide in which the monomolecular decomplexation process is characterized by k_d(298.2 K) = 255 ± 3, 12.3 ± 0.4, and 11.1 ± 0.5 s^{-1}, respectively; $\Delta H_d^* = 56.5 \pm 0.5$, 64.0 ± 0.5, and 65.8 ± 0.9 kJ mol^{-1}, respectively; and $\Delta S_d^* = -9.4 \pm 1.7$, -9.5 ± 1.5, and -4.1 ± 2.6 J K^{-1} mol^{-1}, respectively. In acetonitrile, methanol, and pyridine the exchange rate is in the very slow regime of the ^{23}Na NMR time scale. These data are discussed in terms of the effects of cryptand structure and metal ion and solvent characteristics on cryptate stability and lability.

Introduction

The cryptand 4,7,13,16-tetraoxa-1,10-diazabicyclo[8.8.2]eicosane ($C22C_2$, Chart I) has a clamlike structure in which the two $-(CH_2)_2O(CH_2)_2O(CH_2)_2-$ jaws are hinged about the $>N(CH_2)_2N<$ moiety.[1-6] In alkali-metal $[M.C22C_2]^+$ cryptates a series of bond angle changes have the overall effect of varying the angle between the jaws to give optimal bonding distances appropriate to the nature of M^+ in the solid state.[1,3-5] (Using these crystallographic data, we calculate that the angle between the jaws of $C22C_2$, defined as the dihedral angle between the mean planes delineated by the two hinge nitrogens and the pairs of oxygens in each jaw, is 88.4, 70.9, 89.6, and 100° in the free $C22C_2$, $[Li.C22C_2]^+$, $[Na.C22C_2]^+$, and $[K.C22C_2]^+$, respectively.) This mode of potential metal ion selectivity differs from that exhibited by less flexible cryptands (e.g. $C21C_5$, C211, C221, and C222 shown in Chart I) where the selectivity is predominantly determined by the fit of the metal ion into the approximately spherical cryptand cavity whose size is predetermined by the bicyclic nature of the cryptand.[6-18] Accordingly, it is of considerable interest to investigate the effect of this uncommon characteristic of $C22C_2$ on its selectivity for metal ions in the formation of cryptates in solution. Thus, the stabilities of $[M.C22C_2]^+$, where $M^+ = Na^+$, K^+, Cs^+, and Tl^+, have been determined by potentiometric titration

Chart I. Cryptand Structures

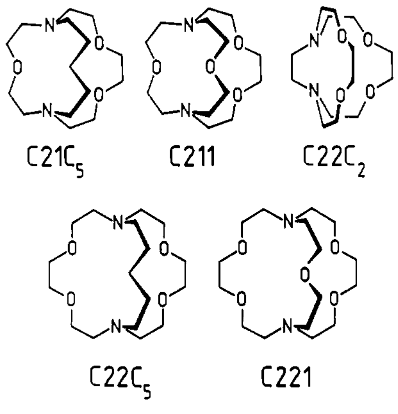

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Table I. Apparent Stability Constants[a] for the Complexation of Li^+, Na^+, K^+, Cs^+, Ag^+, and Tl^+ by 4,7,13,16-Tetraoxa-1,10-diazabicyclo[8.8.2]eicosane ($C22C_2$) at 298.2 K

		log (K/dm^3 mol^{-1})					
solvent	D_N[b]	$[Li.C22C_2]^+$[c]	$[Na.C22C_2]^+$[d]	$[K.C22C_2]^+$[d]	$[Cs.C22C_2]^+$[d]	$[Ag.C22C_2]^+$[c]	$[Tl.C22C_2]^+$[d]
acetonitrile	14.1	7.8 ± 0.1	9.4 ± 0.3	7.2 ± 0.1	5.0 ± 0.1	9.4 ± 0.1	10.4 ± 0.3
water	18.0 (33.0)[e]	<2	3.2 ± 0.1	<2	<2	6.0 ± 0.1	
methanol	19.0 (23.5)[e]	4.0 ± 0.1	6.6 ± 0.1			10.2 ± 0.1	7.8 ± 0.1
dimethyl formamide	26.6	3.5 ± 0.1	6.1 ± 0.1	3.2 ± 0.1	2.7 ± 0.1	9.4 ± 0.1	6.7 ± 0.1
dimethyl sulfoxide	29.8		5.6 ± 0.1				
pyridine	33.1	4.0 ± 0.1	8.4 ± 0.1			5.0 ± 0.1	

[a] In 0.05 mol dm^{-3} Et_4NClO_4 supporting electrolyte. [b] Gutmann donor number from ref 26. [c] Reference 6. [d] This work. [e] In refs 27 and 28 it has been suggested that D_N = 33.0 and 23.5 are more appropriate in water and methanol solutions rather than D_N = 18.0 and 19.0, respectively, obtained for water and methanol in 1,2-dichloroethane solution, where the hydrogen-bonding structure of these solvents is disrupted.

in several solvents to determine the selectivity pattern of $C22C_2$ for monovalent metal ions in conjunction with similar data for Li^+ and Ag^+ from the literature.[6] The rates of Na^+ exchange in $[Na.C22C_2]^+$ in several solvents have also been measured by ^{23}Na NMR spectroscopy to determine the relationship between lability and stability for this cryptate, to determine the effect of metal ion variation on lability through a comparison with exchange rate data for $[Li.C22C_2]^+$, and to facilitate comparison with other cryptates.

Experimental Section

The cryptand $C22C_2$ was prepared as described previously.[1,5] Cesium perchlorate was precipitated from a solution of cesium chloride by the addition of concentrated perchloric acid and was recrystallized from water until chloride was absent. Thallium perchlorate was prepared by reacting thallium carbonate with perchloric acid and was recrystallized from water. Potassium perchlorate (BDH) was recrystallized from water. Sodium perchlorate (Fluka) and silver perchlorate (Aldrich) were used as received after drying. All of the metal perchlorates were vacuum-dried at 353–363 K for 48 h and were then stored over P_2O_5 under vacuum. Deionized water was ultrapurified with a MilliQ-Reagent system to produce water with a resistance of >15 MΩ cm. Acetonitrile, methanol, dimethylformamide, pyridine, and dimethyl sulfoxide were purified and dried by literature methods[19] and were stored under nitrogen over Linde 3-Å molecular sieves in the cases of methanol and acetonitrile and over Linde 4-Å molecular sieves for the other solvents. The water content of these solvents was below the Karl Fischer detection level of approximately 50 ppm. Solutions of anhydrous metal perchlorates and $C22C_2$ were prepared under dry nitrogen in a glovebox. For ^{23}Na 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.

^{23}Na NMR spectra were run at 79.39 MHz on a Bruker CXP-300 spectrometer. An average of 1000 transients was accumulated in a 2048 data point base over an 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[20] on a VAX 11-780 computer to obtain kinetic data. The temperature-dependent ^{23}Na line widths and chemical shifts employed in the line-shape analysis were obtained from a combination of extrapolation from low temperatures where no exchange-induced modification occurred and of line width and chemical shift variations of separate solutions containing either Na^+ or $[Na.C22C_2]^+$ as the only sodium(I) species.

Stability constants for $[Na.C22C_2]^+$ were determined by duplicated potentiometric titrations of 25 cm^3 of 10^{-3} mol dm^{-3} $NaClO_4$ solutions with 10^{-2} mol dm^{-3} $C22C_2$ solutions (except in acetonitrile as is discussed below). The titrations were carried out under dry nitrogen in a thermostated (298.15 ± 0.01 K) titration vessel using a Radiometer G502 Na^+-specific electrode and an Orion Research SA 720 digital analyzer. Stability constants for $[K.C22C_2]^+$ and its Cs^+ and Tl^+ analogues (except in acetonitrile as is discussed below) were determined through duplicate competitive potentiometric titrations of 25 cm^3 of 1.14×10^{-3} mol dm^{-3} $AgClO_4$ solution with a solution 5.44×10^{-2} mol dm^{-3} in both $KClO_4$, $CsClO_4$, or $TlClO_4$ and $C22C_2$ as described in the literature.[16] Due to the low solubility of $KClO_4$ and $CsClO_4$, the stability constants of $[K.C22C_2]^+$ and $[Cs.C22C_2]^+$ in acetonitrile were determined from duplicate titrations of 25 cm^3 of 2.28×10^{-4} mol dm^{-3} $AgClO_4$ solution with a solution 4.97×10^{-3} mol dm^{-3} in both $KClO_4$ or $CsClO_4$ and $C22C_2$. The high stability constants of $[Na.C22C_2]^+$ and $[Tl.C22C_2]^+$ in acetonitrile required a modified method in which a 1.13×10^{-2} mol dm^{-3} $[Ag.C22C_2]^+$ solution was titrated into a 1.49×10^{-3} mol dm^{-3} $NaClO_4$ or $TlClO_4$ solution in the same apparatus used in the previous Ag^+ titrations. The titrations were carried out under dry nitrogen in a thermostated (298.15 ± 0.01 K) titration vessel connected to a thermostated reference vessel by a salt bridge. For a given experiment, the titration and reference vessels and the salt bridge contained solutions made up in the same solvent. The reference and titration electrodes were silver, and the reference solution was 10^{-2} mol dm^{-3} $AgClO_4$ in the solvent under investigation. All titration solutions and that in the salt bridge when used were 0.05 mol dm^{-3} in Et_4NClO_4. An Orion Research SA 720 digital analyzer was also used to measure changes in potential for these titrations.

Results and Discussion

Cryptate Stability. The selectivity of $C22C_2$ for Na^+ is demonstrated by the variation of the stability of $[M.C22C_2]^+$ with M^+ in the sequence $Li^+ < Na^+ > K^+ > Cs^+$ in acetonitrile and dimethylformamide (Table I). It is also coincident with crystallographic observations that the flexible structure of clamlike $C22C_2$ allows a series of bond angle changes that have the cumulative effect of varying the angle between the two jaws hinged about the $>NCH_2CH_2N<$ moiety to fit the size of the complexed cation.[1-5] Thus we have calculated from these crystallographic data that the angle between the jaws of $C22C_2$, defined as the dihedral angle between the mean planes delineated by the two hinge nitrogens and the pairs of oxygens in each jaw, is 88.4, 70.9, 89.6, and 100° in the free $C22C_2$, $[Li.C22C_2]^+$, $[Na.C22C_2]^+$, and $[K.C22C_2]^+$, respectively. It is reasonable to assume that the $[M.C22C_2]^+$ in which the bond angle differs least from that of $C22C_2$ will experience the least strain and an enhanced stability. Thus in $[Li.C22C_2]^+$ this angle is less than that in $C22C_2$ alone and the consequent strain increase has a destabilizing influence on the cryptate. The angle in $[Na.C22C_2]^+$ is similar to that in $C22C_2$, coincident with stability reaching a maximum as a result of strain being at a minimum in this cryptate. In $[K.C22C_2]^+$ the angle increases with cation size beyond that characterizing $C22C_2$ with a corresponding decrease in stability arising from increased strain in this cryptate, and the further decrease in stability for $[Cs.C22C_2]^+$ is probably coincident with a further increase in jaw angle.

In the oxygen donor solvents methanol and dimethylformamide, $[Ag.C22C_2]^+$ and $[Tl.C22C_2]^+$ are more stable than $[Na.C22C_2]^+$ as a result of the lesser ability of these hard-base oxygen donor solvents to compete with $C22C_2$ for the soft acids Ag^+ and Tl^+, which show a preference for nitrogen donor atoms,[21,22] than is the case for hard-acid Na^+. This effect superimposes on the effect of cation size. In the softer base nitrogen donor solvent acetonitrile, this competition changes and results in an increase in the stability of $[Na.C22C_2]^+$, which becomes similar to that of $[Ag.C22C_2]^+$. The greater stability of $[Ag.C22C_2]^+$ by comparison with [Tl.

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Table II. Apparent Stability Constants of Monovalent Metal Ion Cryptates in Dimethylformamide at 298.2 K

		log (K/dm^3 mol^{-1})				
M	r,[a] Å	$[M.C21C_5]^+$	$[M.C211]^+$	$[M.C22C_2]^+$	$[M.C22C_5]^+$	$[M.C221]^+$
Li	0.76	1.80[b]	6.9[c]	3.5[d]		3.58[c]
Na	1.02	2.87[e]	5.23[c]	6.1[f]	3.66[g]	7.93[c]
K	1.38		<2.5[c]	3.2[f]		6.66[c]
Rb	1.52					5.35[c]
Cs	1.67			2.7[f]		3.61[c]
Ag	1.15	4.29[b]	8.60[c]	9.4[d]		12.41[c]
Tl	1.50		3.15[c]	6.7[f]		8.61[c]

[a] Reference 23. [b] Reference 9. [c] Reference 16. [d] Reference 6. [e] Reference 13. [f] This work. [g] Reference 33.

$C22C_2]^+$ in methanol and dimethylformamide probably reflects the larger size of Tl^+ (r = 1.50 Å)[23] by comparison with Ag^+ (r = 1.15 Å) and hence greater strain in $[Tl.C22C_2]^+$, and also the softer acid character of Ag^+ by comparison with Tl^+, which has properties somewhere between those of Ag^+ and the hard acid K^+.[24,25] On this basis, the greater stability of $[Tl.C22C_2]^+$ compared with that of $[Ag.C22C_2]^+$ in acetonitrile is attributable to the softer base character of this nitrogen donor solvent by comparison with oxygen donor solvents. In acetonitrile the stabilities of the alkali-metal $[M.C22C_2]^+$ cryptates increase substantially in both absolute and relative terms by comparison with $[Ag.C22C_2]^+$ as a consequence of this nitrogen donor solvent competing less strongly with $C22C_2$ for the alkali-metal ions than can an oxygen donor solvent. It might be expected by the same argument acetonitrile should compete more strongly for Ag^+ than does dimethylformamide, but it appears that this effect is counterbalanced by the greater electron-donating ability of dimethylformamide, as indicated by its Gutmann donor number, D_N,[26-28] and as a result the variation in the stability of $[Ag.C22C_2]^+$ in the two solvents is small.

The stabilities of $[Li.C22C_2]^+$ and $[Na.C22C_2]^+$ tend to decrease as the solvent D_N increases, consistent with a more strongly electron-donating solvent competing more effectively with $C22C_2$ for Li^+ and Na^+ (Table I). The apparently anomalous position of water in the sequence is resolved when a D_N value of 33.0 determined in aqueous solution is employed, which is probably more appropriate to aqueous solutions generally than D_N = 18.0 obtained in 1,2-dichloroethane solution, where the hydrogen bonding of water is disrupted.[26-28] The stabilities of $[Li.C22C_2]^+$ and $[Na.C22C_2]^+$ are higher than expected in pyridine for D_N = 33.1. This may indicate that the incorporation of the nitrogen donor atom in the ring structure results in steric hindrance between adjacent pyridines in the Na^+ solvation shell, which effectively decreases the solvating power of pyridine and disrupts the relationships between oxygen and nitrogen donor solvents and the stabilities of the alkali-metal cryptates discussed earlier for less hindered dimethylformamide and acetonitrile. However, the stability of $[Ag.C22C_2]^+$ is lower in pyridine than in the weaker nitrogen donor acetonitrile, which probably reflects the tendency of Ag^+ to form two strong bonds in a linear array[21] with the consequence that the effect of the steric crowding becomes less significant. The variations in stability with solvent are similar for $[Li.C22C_2]^+$ and $[Na.C22C_2]^+$, indicating that the dominant factors controlling their stabilities are similar.

The variation of the stability of several different cryptates with M^+ in dimethylformamide is shown Table II. Generally, the sequence of cryptate stability, as exemplified by $[Li.C211]^+ > [Li.C221]^+ > [Li.C22C_2]^+ > [Li.C21C_5]^+$, may be interpreted in terms of a combination of the fit of M^+ into the cryptand cavity and the number of cryptand donor atoms interacting with M^+. Thus $[Li.C211]^+$ has the highest stability as a consequence of the optimal fit of Li^+ into the C211 cavity to form an inclusive cryptate (where Li^+ is at the center of the cryptand cavity) and the interaction of Li^+ with six donor atoms.[10,29] The fit of Li^+ into the larger C221 is no longer optimal, and consequently stability decreases further in $[Li.C221]^+$ despite the presence of seven donor atoms. In contrast, $C22C_2$ can adjust its cavity size by variation of the jaw angle to an optimal fit for Li^+ so that $[Li.C22C_2]^+$ is similar in stability to $[Li.C221]^+$, despite the presence of only six donor atoms in $C22C_2$. In $[Li.C21C_5]^+$ an optimal fit of Li^+ into the $C21C_5$ cavity also occurs but the decrease in the number of donor atoms to 5 results in this cryptate existing substantially in the exclusive form in solution (in contrast to the solid state, where it exists in the inclusive form) with a consequent decrease in overall stability.[7,30]

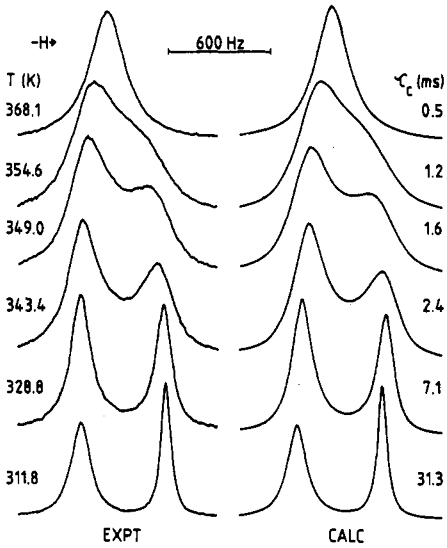

Figure 1. Typical exchange-modified 79.39-MHz ^{23}Na NMR spectra of a dimethylformamide solution of solvated Na^+ (0.041 mol dm^{-3}) and $[Na.C22C_2]^+$ (0.059 mol dm^{-3}). Experimental temperatures and spectra appear to the left of the figure, and the best fit calculated line shapes and corresponding τ_c values appear to the right. The resonance of $[Na.C22C_2]^+$ appears downfield from that of solvated Na^+.

For the larger Na^+ the sequence of stability changes to $[Na.C221]^+ > [Na.C22C_2]^+ > [Na.C211]^+ > [Na.C22C_5]^+ > [Na.C21C_5]^+$, consistent with Na^+ being too large to enter the $C21C_5$ and C211 cavities so that their cryptates are exclusive in structure (where Na^+ resides outside the cryptand cavity)[31] and markedly less stable than inclusive $[Na.C221]^+$, where Na^+ fits the cryptand cavity optimally.[32] The second most stable cryptate in the series is $[Na.C22C_2]^+$ (which is also the most stable of the

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Table III. Sodium Ion Exchange on $[\mathrm{Na.C22C_2}]^+$ in Water, Dimethylformamide, and Dimethyl Sulfoxide: Solution Composition and Kinetic Parameters[a]

soln	solvent	$[\mathrm{Na^+_{solvated}}]$, mol dm^{-3}	$[\mathrm{Na.C22C_2{}^+}]$, mol dm^{-3}	$k_d(T)$, s^{-1}	k_d(298.2 K), s^{-1}	ΔH_d^*, kJ mol^{-1}	ΔS_d^*, J K^{-1} mol^{-1}
				k_d(309.6 K)			
i	water	0.0360	0.0177	621 ± 7	254 ± 5	57.1 ± 1.1	−7.5 ± 3.3
ii		0.0307	0.0231	632 ± 7	264 ± 5	55.7 ± 0.8	−11.7 ± 2.5
iii		0.0204	0.0333	606 ± 5	249 ± 4	56.8 ± 0.8	−8.5 ± 2.5
i–iii[b]				619 ± 4	255 ± 3	56.6 ± 0.5	−9.4 ± 1.7
				k_d(351.2 K)			
i	dimethylformamide	0.076	0.024	721 ± 7	12.3 ± 0.7	64.1 ± 0.9	−20.6 ± 1.3
ii		0.059	0.041	727 ± 4	12.8 ± 0.3	63.6 ± 0.4	−9.0 ± 2.5
iii		0.041	0.059	701 ± 7	12.9 ± 0.7	62.9 ± 0.9	−10.5 ± 1.3
iv		0.035	0.065	743 ± 3	11.0 ± 0.3	66.4 ± 0.5	−12.7 ± 2.9
i–iv[b]				717 ± 4	12.3 ± 0.4	64.0 ± 0.5	−9.5 ± 1.5
				k_d(334.4 K)			
i	dimethyl sulfoxide	0.0675	0.0333	227 ± 4	10.7 ± 0.6	67.4 ± 1.2	0.7 ± 3.4
ii		0.0504	0.0504	221 ± 5	11.7 ± 0.7	64.6 ± 1.3	−7.9 ± 3.5
iii		0.0343	0.0665	219 ± 7	10.6 ± 0.9	66.7 ± 2.0	−1.6 ± 5.8
i–iii[b]				222 ± 3	11.1 ± 0.5	65.8 ± 0.9	−4.1 ± 2.6

[a] Errors represent one standard deviation from the least-squares fit of the experimental τ_c data to eq 2. [b] Simultaneous fit of all data for this solvent.

alkali-metal $[\mathrm{M.C22C_2}]^+$ series) as a consequence of optimization of fit of $\mathrm{Na^+}$ and minimization of strain in $\mathrm{C22C_2}$. Six donor atoms are present in $[\mathrm{Na.C22C_5}]^+$, but in the solid state $\mathrm{Na^+}$ only has a significant bonding interaction with the four oxygen atoms at an average distance of 2.436 Å (with which it shares a common plane) and is an average distance of 3.014 Å from the two nitrogen atoms,[33] unlike the case of $[\mathrm{Na.C22C_2}]^+$, where all six donor atoms are at bonding distances. This difference probably accounts for the lower stability of $[\mathrm{Na.C22C_5}]^+$. As the size of $\mathrm{M^+}$ increases further, it is seen that the stabilities of $[\mathrm{M.C22C_2}]^+$ and $[\mathrm{M.C221}]^+$ decrease and become more similar, consistent with specific interactions becoming less important as the sizes of $\mathrm{M^+}$ and the cryptand cavity become increasingly dissimilar.

Cryptate Lability. Complete line-shape analysis[20] of the temperature-dependent coalescence of the $^{23}\mathrm{Na}$ resonances arising from solvated $\mathrm{Na^+}$ and $[\mathrm{Na.C22C_2}]^+$ (Figure 1) in water, dimethylformamide, and dimethyl sulfoxide yields τ_c, the mean lifetime of $\mathrm{Na^+}$ in $[\mathrm{Na.C22C_2}]^+$, for solutions whose compositions are given in Table III. (For a given solution, $\tau_c/X_c = \tau_s/X_s$, where τ_s is the mean lifetime of $\mathrm{Na^+}$ in the fully solvated state and X_c and X_s are the corresponding mole fractions.) The magnitudes and temperature variations of τ_c for each of the solutions studied for a given solvent are very similar (Figure 2). This indicates that the mean lifetime of $[\mathrm{Na.C22C_2}]^+$, τ_c ($=1/k_d$, where k_d is the decomplexation rate constant), is independent of the concentration of solvated $\mathrm{Na^+}$ (Table III), consistent with the nonparticipation of solvated $\mathrm{Na^+}$ in the rate-determining step of the predominant pathway for $\mathrm{Na^+}$ exchange on $[\mathrm{Na.C22C_2}]^+$ and the operation of a monomolecular mechanism for the decomplexation of $\mathrm{Na^+}$ from the cryptand as shown in eq 1, where k_c is the complexation rate constant. The kinetic parameters for the decomplexation of $[\mathrm{Na.C22C_2}]^+$ (Table III) are derived from the temperature variation of τ_c through eq 2, in which all symbols

$$\mathrm{Na^+ + C22C_2 \underset{k_d}{\overset{k_c}{\rightleftharpoons}} [Na.C22C_2]^+} \tag{1}$$

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

have their usual meaning. The rate of exchange of $\mathrm{Na^+}$ between the solvated and $[\mathrm{Na.C22C_2}]^+$ environments is too slow to cause any significant broadening of the separate $^{23}\mathrm{Na}$ resonances characterizing these environments close to the boiling point temperatures in acetonitrile (355 K), methanol (338 K), and pyridine (388 K). (Conservative lower limits for τ_c at these temperatures of ca. 180, 70, and 70 ms may be estimated in acetonitrile, methanol, and pyridine, respectively, by calculating the τ_c value consistent with a broadening of the $[\mathrm{Na.C22C_2}]^+$ observed resonance width by a factor of 1.5.[18]) This variation in lability with the nature of the solvent is similar to that observed for other sodium(I) cryptates for which it is generally found that the magnitude of k_d(298.2 K) increases with change of solvent in the sequence methanol < dimethylformamide < water. This is also consistent with a tendency for k_d to increase with solvent D_N and to be much more dependent on the nature of the solvent than is k_c, which suggests that the transition state is more similar to the solvated metal ion and the free cryptand than to the cryptate.[9,14,16] The data obtained in aqueous solution tend to diverge from this generalization, with k_c usually being substantially less than those determined in other solvents, as is seen for $[\mathrm{Na.C22C_2}]^+$ and $[\mathrm{Na.C211}]^+$ (Table IV). This may be a consequence of a combination of more extensive solvation of the metal ion, cryptand, and cryptate by comparison with other solvents arising from the relatively small molecular size of water and its greater hydrogen-bonding ability by comparison with other solvents.

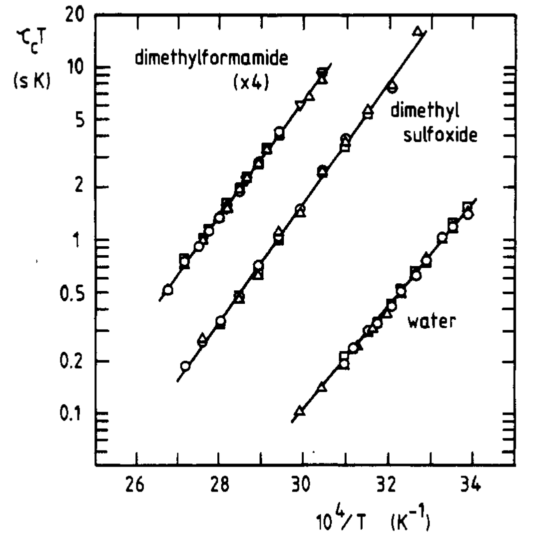

Figure 2. Temperature variation of τ_c for $[\mathrm{Na.C22C_2}]^+$ in water, dimethylformamide, and dimethyl sulfoxide. Data points for aqueous solutions i–iii are represented by triangles, squares, and circles, respectively. Data points for dimethylformamide solutions i–iv are represented by triangles, squares, inverted triangles, and circles, respectively. Data points for dimethyl sulfoxide solutions i–iii are represented by triangles, squares, and circles, respectively. The solid lines represent the best fits of the combined data for each group of solutions to eq 2.

The $[\mathrm{Na.C22C_2}]^+$ kinetic data may be compared with those characterizing $[\mathrm{Li.C22C_2}]^+$, $[\mathrm{Na.C21C_5}]^+$, $[\mathrm{Na.C211}]^+$, $[\mathrm{Na.C22C_5}]^+$, and $[\mathrm{Na.C221}]^+$, for which monomolecular decomplexation mechanisms also operate in the solvents listed in Table

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(33) Clarke, P.; Lincoln, S. F.; Tiekink, E. R. T. *Inorg. Chem.*, in press.

Table IV. Kinetic Parameters for Na^+ Exchange on $[Na.C22C_2]^+$ and Other Cryptates

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}	$\Delta H_d^\ddagger$, kJ mol^{-1}	$\Delta S_d^\ddagger$, J $K^{-1}\ mol^{-1}$
		$[Na.C22C_2]^{+c}$			
methanol	19.0 $(23.5)^d$		small		
water	18 $(33.0)^d$	4.04	255	56.5	-9.4
dimethylformamide	26.6	155	12.3	64.0	-9.5
dimethyl sulfoxide	29.8	44.2	11.1	65.8	-4.1
		$[Li.C22C_2]^{+e}$			
methanol	19.0 $(23.5)^d$	97.1	971	31.0	-84.0
dimethylformamide	26.6	7.60	240	22.5	-124
		$[Na.C21C_5]^{+f}$			
methanol	19.0 $(23.5)^d$	104	1800	44.9	-31.9
dimethylformamide	26.6	214	28800	40.0	-25.3
		$[Na.C211]^{+g}$			
methanol	19.0 $(23.5)^d$	31.0	2.5		
water	18 $(33.0)^d$	0.754	47.7	67.2	12.6
dimethylformamide	26.6	19.2	12.1	83.5	55.8
dimethyl sulfoxide	29.8	14.5	34.0	69.5	17.4
		$[Na.C22C_5]^{+h}$			
methanol	19.0 $(23.5)^d$	520	41.0	55.1	-29.2
		$[Na.C221]^{+i}$			
methanol	19.0 $(23.5)^d$	1700	0.0235		
dimethylformamide	26.6	180	0.25		

[a] Gutmann donor numbers from ref 26. [b] $k_c = Kk_d$. [c] This work. [d] In refs 27 and 28 it has been suggested that D_N = 23.5 and 33.0 are more appropriate in methanol and water solutions than D_N = 19.0 and 18.0, respectively, obtained for methanol and water in 1,2-dichloroethane solution, where the hydrogen-bonding structure of these solvents is disrupted. [e] Data from ref 6. [f] Data from ref 14. [g] Data from ref 13. [h] Data from ref 33. [i] Data from ref 16.

IV.[6,14,33] (Sometimes, a bimolecular exchange mechanism operates as observed for $[Li.C221]^+$ in acetonitrile and propylene carbonate, consistent with solvents of higher dielectric constants favoring a bimolecular transition state for some cryptates.[12]) Dimethylformamide is the only solvent for which quantitative data are available for both $[Na.C22C_2]^+$ and $[Li.C22C_2]^+$, and it is seen that the greater stability of $[Na.C22C_2]^+$ at 298.2 K is a consequence of its larger k_c and smaller k_d. This smaller k_d arises from the larger $\Delta H_d^\ddagger$ characterizing $[Na.C22C_2]^+$. It is likely that the greater strain in $[Li.C22C_2]^+$ (discussed above) labilizes this cryptate toward decomplexation relative to $[Na.C22C_2]^+$ such that it is characterized by a larger k_d and a much smaller $\Delta H_d^\ddagger$. This smaller $\Delta H_d^\ddagger$ probably arises from a combination of the release of strain in bound $C22C_2$ as it approaches the free $C22C_2$ geometry in the transition state and the partial resolvation of Li^+ in the transition state. It is seen from the space-filling representation of $[Li.C22C_2]^+$ (Figure 3) that Li^+ is deep in the $C22C_2$ "throat" and unlikely to interact substantially with solvent. Thus some of the considerable negative $\Delta S_d^\ddagger$ characterizing $[Li.C22C_2]^+$ probably arises from the partial resolvation of Li^+ as the transition state forms. In contrast, the lower strain and wider jaw angle of bound $C22C_2$ together with the probably incomplete desolvation of Na^+ in the $[Na.C22C_2]^+$ ground state results in a larger $\Delta H_d^\ddagger$ due to a lesser release of strain and a lesser enthalpic contribution from resolvation of the larger and partially solvated Na^+ to form the transition state.[34] The smaller negative $\Delta S_d^\ddagger$ characterizing $[Na.C22C_2]^+$ is attributable to Na^+ already being partially solvated in the ground state. These arguments are also consistent with the complexation of Na^+ by $C22C_2$ being characterized by a larger k_c than is the complexation of Li^+.

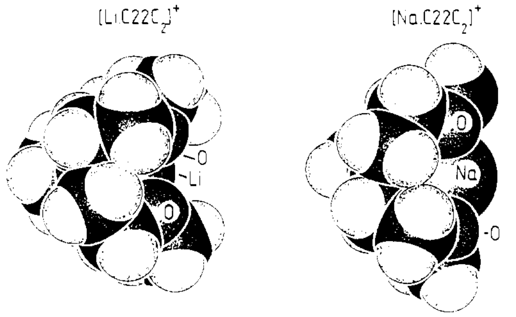

Figure 3. Space-filling representations of $[Li.C22C_2]^+$ and $[Na.C22C_2]^+$ generated from the crystal structures[3,4] by the program SCHAKAL (Keller, E. SCHAKAL. Inorganic Chemistry Institute, University of Freiburg, Freiburg, Germany) using spheres of appropriate radii.

In water, dimethylformamide, and dimethyl sulfoxide k_d characterizing $[Na.C211]^+$ ranges from being 0.19 to 3 times k_d characterizing $[Na.C22C_2]^+$ (which has the same number of donor atoms), but k_c characterizing $[Na.C22C_2]^+$ is the larger in each case such that K is similar to or greater than that characterizing $[Na.C211]^+$. The larger k_c characterizing $[Na.C22C_2]^+$ may reflect more cooperativity in the desolvation and complexation of Na^+ arising from the greater flexibility of $C22C_2$. The presence of only five donor atoms in $C21C_5$ results in $[Na.C21C_5]^+$ being substantially more labile in dimethylformamide than $[Na.C22C_2]^+$, particularly toward decomplexation, which is attributable to the decreased electrostatic interaction between Na^+ and $C21C_5$.[14] The increase in the number of donor atoms to 7 and the concomitant increase of cavity size of C221 result in k_d characterizing inclusive $[Na.C221]^+$ being 0.06 times that of $[Na.C22C_2]^+$ in dimethylformamide, and as a consequence

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(34) In the solid state Na^+ is bound by the six $C22C_2$ donor atoms and one NCS^- in $[Na.C22C_2.NCS]$ and is 7-coordinate, while Li^+ is 6-coordinate in $[Li.C22C_2]NCS$, being bound by the $C22C_2$ donor atoms only.[1,3,4] If these coordination numbers are retained in solution, Na^+ in $[Na.C22C_2]^+$ will coordinate a solvent molecule in the ground state, while Li^+ in $[Li.C22C_5]^+$ will not.

$[Na.C221]^+$ is substantially more stable than $[Na.C22C_2]^+$.

Conclusion

The variation of the stability of $[M.C22C_2]^+$ with M^+ in the sequence $Li^+ < Na^+ > K^+ > Cs^+$ is consistent with the flexible structure of clamlike $C22C_2$ allowing the angle between its two jaws hinged about the $>NCH_2CH_2N<$ moiety to vary with the size of the complexed M^+ such that optimum bonding distances and a minimization of strain are achieved in $[Na.C22C_2]^+$. Although this metal ion selection mode of $C22C_2$ differs from that of less flexible cryptands, the magnitudes of the stability constants and kinetic parameters are within the range arising from the interplay of the effects of the number of donor atoms and cryptand flexibility, which produce variations in cryptate stability and lability generally.

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Bidentate Phosphine Basicities As Determined by Enthalpies of Protonation

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Enthalpies for both the first (ΔH_{HP1}) and the second (ΔH_{HP2}) protonations of the phosphorus donors in bidentate phosphines have been determined by titration calorimetry using CF_3SO_3H in 1,2-dichloroethane solvent. The ΔH_{HP1} values for the series $Ph_2P(CH_2)_nPPh_2$, $n = 1$–6, range from -22.0 ± 0.1 kcal mol^{-1} for $n = 1$ to -25.2 ± 0.1 kcal mol^{-1} for $n = 6$. The ΔH_{HP2} values also become more exothermic from −14.9 ● 0.2 to −24.9 ● 0.1 kcal mol^{-1} with increasing alkyl chain length. The ΔH_{HP1} and ΔH_{HP2} values for other bidentates, $Ph_2P(bridge)EPh_2$ (E = P, bridge = *cis*-CH=CH, *trans*-CH=CH, 1,2-C_6H_4; E = As, bridge = CH_2CH_2) and $Me_2PCH_2PMe_2$, have also been determined. Correlations of ΔH_{HP1} and ΔH_{HP2} with the corresponding pK_{a1} and pK_{a2} values taken from the literature are presented.

Introduction

Bidentate and monodentate phosphines are common ligands in organometallic and coordination chemistry.[1] Much effort has been directed toward understanding the effects of monodentate phosphines on properties of metal complexes. For example, Giering,[2a] Poë,[2b] and co-workers have recently introduced an approach to the quantitative analysis of ligand effects (QALE) using the steric and electronic properties of phosphorus(III) ligands. Relatively few studies, however, have focused on the relationship between the properties of bidentate ligands and the properties of their metal complexes.[3,4]

Table I. ΔH_{HP1}, ΔH_{HP2} and pK_{a1}, pK_{a2} Values for Bidentate Phosphines

phosphine	$-\Delta H_{HP1}$,[a] kcal mol^{-1}	pK_{a1}[b]	$-\Delta H_{HP2}$,[c] kcal mol^{-1}	pK_{a2}[b]
$Ph_2PCH_2PPh_2$ (dppm)	22.0 (±0.1)	3.81	14.9 (±0.2)	−2.73
$Ph_2P(CH_2)_2PPh_2$ (dppe)	22.8 (±0.2)	3.86	20.2 (±0.1)	0.99
$Ph_2P(CH_2)_3PPh_2$ (dppp)	23.4 (±0.1)	4.50	22.4 (±0.3)	2.53
$Ph_2P(CH_2)_4PPh_2$ (dppb)	24.6 (±0.1)	4.72[f]	23.8 (±0.2)	4.28[f]
$Ph_2P(CH_2)_5PPh_2$ (dppent)	24.8 (±0.2)	4.84[f]	24.5 (±0.1)	4.67[f]
$Ph_2P(CH_2)_6PPh_2$ (dpph)	25.2 (±0.1)	5.05[f]	24.9 (±0.1)	4.89[f]
cis-$Ph_2P(CH{=}CH)PPh_2$ (*cis*-dppv)	19.9 (±0.3)	2.27	10.0 (±0.2)	
trans-$Ph_2P(CH{=}CH)PPh_2$ (*trans*-dppv)	21.7 (±0.2)	2.74	12.7 (±0.1)	
$Ph_2P(1,2\text{-}C_6H_4)PPh_2$ (dppbz)	21.3 (±0.1)	2.91[f]	10.7 (±0.3)	
$Ph_2P(CH_2)_2AsPh_2$ (arphos)	23.2 (±0.4)	3.96[f]	8.2 (±0.1)	
$Me_2PCH_2PMe_2$ (dmpm)	31.0 (±0.3)	8.24[f]	25.8 (±0.2)	
$Et_2P(CH_2)_2PEt_2$ (depe)	31.3[f]	8.41[b]		5.04[b]
$(p\text{-}CF_3C_6H_4)_3P$	13.6 (±0.2)[d]	−1.32[f]		
PPh_3	21.2 (±0.1)[d,e]	2.73[e]		
PPh_2Me	24.7 (±0.0)[d,e]	4.59[e]		
PMe_3	31.6 (±0.2)[d,e]	8.65[e]		

[a] For protonation with 1 equiv of CF_3SO_3H in DCE solvent at 25.0 °C. [b] Reference 10. [c] For addition of a second equivalent of CF_3SO_3H in DCE solvent at 25.0 °C. [d] ΔH_{HP}, eq 1. [e] Selected from ref 5. [f] Calculated from eq 7.

Previously, Bush and Angelici[5] measured the enthalpies of protonation (ΔH_{HP}, eq 1) of several aryl-, mixed alkyl-/aryl-, and alkylphosphines with 0.1 M CF_3SO_3H in 1,2-dichloroethane (DCE) solution. These ΔH_{HP} values are a quantitative measure

$$PR_3 + CF_3SO_3H \xrightarrow[25.0\ ^\circ C]{DCE} HPR_3^+CF_3SO_3^-;\quad \Delta H_{HP} \qquad (1)$$

of the basicities or σ-donor abilities of these monodentate phosphines. In this paper, we report the basicities of several bidentate phosphines as determined by their enthalpies of protonation with 0.1 M CF_3SO_3H in DCE. For the dibasic phosphines, which are listed with their abbreviations in Table I, ΔH_{HP1} represents the heat liberated during the addition of the first equivalent of acid, while ΔH_{HP2} is the enthalpy of reaction for the addition of a second equivalent of acid. The protonation reactions occurring in these solutions are given in eqs 2 and 3 but do not necessarily represent

$$P\frown P + CF_3SO_3H \xrightarrow[25.0\ ^\circ C]{DCE} HP\frown P^+CF_3SO_3^- \qquad (2)$$

$$HP\frown P^+CF_3SO_3^- + CF_3SO_3H \xrightarrow[25.0\ ^\circ C]{DCE} HP\frown PH^{2+}(CF_3SO_3^-)_2 \qquad (3)$$

ΔH_{HP1} and ΔH_{HP2}, respectively, as will be discussed. The results of these studies give a quantitative measure (ΔH_{HP1} and ΔH_{HP2}) of the σ-donor properties of bidentate phosphine ligands.

The studies presented herein are part of a program aimed at determining the quantitative effects of ligands on the basicities of transition-metal complexes (eq 4). We have already reported[6]

$$ML_x + CF_3SO_3H \xrightarrow[25.0\ ^\circ C]{DCE} HML_x^+CF_3SO_3^-;\quad \Delta H_{HM} \qquad (4)$$

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