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Effects of Substituents on the Stability and Kinetics of Alkali Metal Cryptates in Methanol

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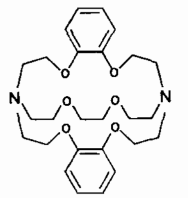
The stability constants and the exchange kinetics of alkali metal complexes with the cryptands $(2_D, 2, 2)$ *and* $(2_B, 2_B, 2)$ *have been measured in methanol and compared with previous results for* (2, 2, 2) *and* $(2_B, 2, 2)$*. The effects of the alkyl chain (D) and the benzo group (B) substituents is a reduction in the cryptate stabilities and an increase in the decomplexation rates. We have found that the decrease of the cavity size in the sequence* $(2, 2, 2) > (2_D, 2, 2) > (2_B, 2, 2) > (2_B, 2_B, 2)$ *has a remarkable influence on the entropies of complex formation and the activation entropies for the dissociation process.*

Introduction

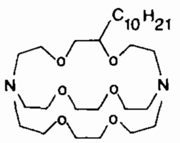
Cryptands are cavity containing macromolecules which form stable complexes with alkali metal ions [1]. For a given cation, the stability constant is largest for the cation which fits best into the cavity of the ligand. Thus stability maxima are found for $Li(2,1,1)^+$, $Na(2,2,1)^+$, and $K(2,2,2)^+$. Correspondingly the dissociation rates of these complexes are lower than those of other alkali cryptates. Because of the rigidity of cryptands, the stability constants of the cryptates for a given cation depend strongly on the particular cryptand molecule involved. Therefore, cryptate stabilities and dissociation rates should be strongly influenced by substituents on the ligand.

In this paper we report the results of our studies on the kinetics and thermodynamics of complex formation between alkali metal ions and the cryptands $(2_B, 2_B, 2)$ (I) and $(2_D, 2, 2)$ (II). The data are compared with previous results on alkali metal (2, 2, 2) and $(2_B, 2, 2)$ cryptates [2, 3]. It is shown that the substituents reduce the stability constants by a cooperative action of reducing the formation rates, and increasing the dissociation rates.



$(2_B,2_B,2)$

(I)



$(2_D,2,2)$

(II)

Experimental

The commercial samples (Merck) of $(2_D, 2, 2)$ and $(2_B, 2_B, 2)$ were found to be of sufficient purity. Details of purification of methanol, potentiometric measurements of stability constants and determinations of heats of complex formation, both at 25 °C, were the same as described earlier [2, 3]. The stability constants of the alkali metal complexes have been determined indirectly by competition [2] with Ag^+ using the stability constants of the corresponding silver cryptates: $\log K_s = 11.8$ for $(2_B, 2_B, 2)$ and $\log K_s = 11.9$ for $(2_D, 2, 2)$. The decomplexation kinetic was measured in a stopped-flow apparatus with conductance detection under pseudo-first-order conditions using an excess of trifluoromethanesulfonic acid [2, 3].

Results and Discussion

Cryptands with less than three oxygen atoms in the chains linking the nitrogen atoms are quite rigid molecules, and are able to discriminate much more effectively between different cations than most monocyclic ligands [4]. Therefore both stability constants and rate constants for cryptate complexes are expected to be strongly influenced by different

TABLE I. Stability and Rate Constants of Alkali Metal Cryptates in Methanol at 25 °C.

M^+	$\log K_s$[a]		$\log k_d$[b]		$\log k_f$	
	$(2_B, 2_B, 2)$	$(2_D, 2, 2)$	$(2_B, 2_B, 2)$	$(2_D, 2, 2)$	$(2_B, 2_B, 2)$	$(2_D, 2, 2)$
Li^+	2.0; 2.3[c]	2.0				
Na^+	7.60	7.0	0.09	0.57	7.69	7.62
K^+	8.74	9.42	−0.57	−1.33	8.17	8.09
Rb^+	5.91	7.61	2.11	−0.27	8.03	7.87
Cs^+	2.61	3.21				

[a] The precision of $\log K_s$ is ±0.05. [b] The precision of $\log k_d$ is ± 0.01. [c] J. M. Lehn, *Struct. Bonding (Berlin)*, *16*, 1 (1973).

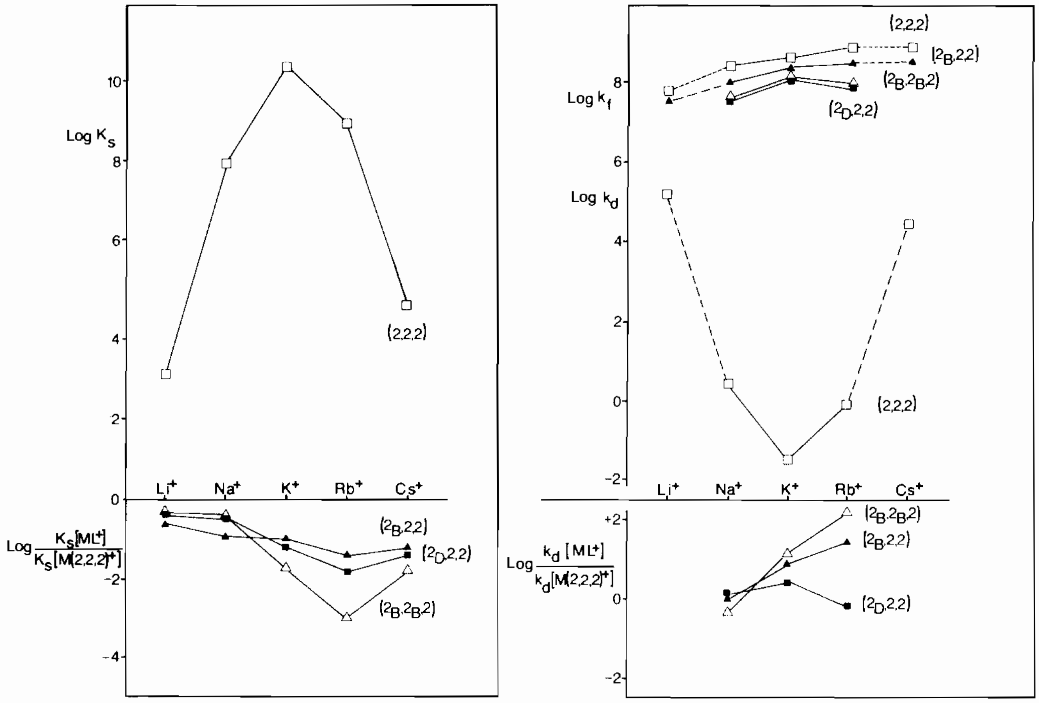


Fig. 1. Stability constants ($\log K_s$) and rates of dissociation ($\log k_d$) and of formation ($\log k_f$) for alkali metal cryptates with (2, 2, 2) and changes in $\log K_s$ and $\log k_d$ by substituents on (2, 2, 2) in methanol at 25 °C.

substituents introduced in the cryptand's chains. We have investigated the effect of two types of substituent on the complexing properties of (2, 2, 2): a benzene ring, which should mainly affect the properties in the cavity region, and a long-chain alkyl group ($-C_{10}H_{22}$), whose mobility in solution may influence more specifically the outer sphere region of (2, 2, 2).

Stability Constants and Rate Constants

The stability constants, K_s, and the rates of dissociation, k_d, and formation, k_f, of the complexes are interrelated by

$$K_s = k_f/k_d, \qquad (1)$$

so that the substituent effects cannot be interpreted independently for all three quantities. As will be shown, k_d values have a much more specific dependence on the ions involved than k_f values and, therefore, k_d and K_s values will be treated jointly.

The stability and rate constants of alkali complexes with $(2_D, 2, 2)$ and $(2_B, 2_B, 2)$ are collected in Table I, and are presented graphically in Fig. 1, together with the results of previous investigations [2, 3]. In Fig. 1 the effects of the substituents on the properties of the (2, 2, 2) complexes are shown as differences between the corresponding quantities for the various ions.

The overall effect of the substituents is to increase the rate of dissociation, k_d, and to reduce the rate of formation, k_f, both of which lead to a reduction in the stability constant, K_s. It is also found that the substituent's effect on both k_d and K_s depends in a specific way on the ions involved, but that the k_f values show more general trends with substitution.

The effects of benzo group substitution in the ligands are (a) to diminish the cavity volume of (2, 2, 2), since the distance between the two oxygen atoms joined to the benzene ring is shorter than that in an unsubstituted chain, (b) to weaken the electronegativity of these oxygen atoms, (c) to reduce the flexibility of the ligand.

For K^+ and larger cations, all of these effects should tend to reduce the stability of the complexes, whereas for Na^+ and Li^+, effect (a) should help to increase the stabilities of the complexes. It may be seen from Fig. 1 that K_s and k_d values have a similar dependence upon ion size, and in all cases have extrema for the K^+ ion. This general dependence upon size then is unchanged upon benzo-substitution, but because of factors (a)–(c) above, K_s is progressively reduced and k_d increased on going from (2, 2, 2) to (2_B, 2, 2) and to (2_B, 2_B, 2). The same is not true for K_s and k_d values for Na^+, and K_s values for Li^+. Thus for these cations the (2_B, 2_B, 2) complexes are slightly more stable than those of (2_B, 2, 2), and k_d for $Na(2_B, 2_B, 2)^+$ is smaller than that of $Na(2_B, 2, 2)^+$. Both of these results suggest that the two benzene rings in (2_B, 2_B, 2) reduce the cavity volume of (2, 2, 2) to a size which is more appropriate for Na^+ and Li^+ than that of (2_B, 2, 2). The details of these substituent effects are, however, somewhat dependent upon the solvent. Thus in propylene carbonate [4] addition of benzene rings actually causes a shift in the stability maximum from K^+ to Na^+, but there is an accompanying decrease in all stability constants, which is larger for (2_B, 2_B, 2) than for (2_B, 2, 2).

The other substituent, an alkyl chain ($-C_{10}H_{21}$), also reduces the stabilities of the $M(2, 2, 2)^+$ complexes, but without any ion specificity, as only the formation rates are significantly affected. Strikingly, the dissociation rates for the Na^+ cryptates of (2, 2, 2), (2_D, 2, 2), and (2_B, 2, 2) are almost identical. Only for $Na(2_B, 2_B, 2)^+$ is there a significant reduction in k_d, presumably because of the reduction in cavity volume, towards the result for $Na(2, 2, 1)^+$ [5].

The effect of substituents on the rates of complex formation k_f is much less specific than on k_d (Fig. 1). For all of the ions studied, k_f decreases in the order $(2, 2, 2) > (2_B, 2, 2) > (2_B, 2_B, 2) > (2_D, 2, 2)$, although formation rates for the last two are practically identical. It is also found that k_f values for (2_B, 2_B, 2) and (2_B, 2, 2) cryptates do not show the linear dependence of log k_f on the reciprocal ionic radius, as was previously found for (2, 2, 2) and (2_B, 2, 2) cryptates. Thus, k_f values for K^+ complexes of (2_B, 2_B, 2) and (2_D, 2, 2) are larger than those of the adjacent cations, and preclude an extrapolation of log k_f to give a value of Cs^+.

TABLE II. Rate Constants for Dissociation and Proton Catalysis of Some Na^+-cryptates in Methanol at 25 °C.

Cry	k_d [s^{-1}]	k_{H^+} [M^{-1} s^{-1}]	k_{H^+}/k_d [M^{-1}]
(2_D, 2, 2)	3.67	9.4×10^2	256
(2, 2, 2)	2.87	4.2×10^2	146
(2_B, 2, 2)	2.74	2.7×10^2	99
(2_B, 2_B, 2)	1.23	0.87×10^2	71

A dependence of the experimental dissociation rate constants, k_e, on proton concentration was found only for Na^+ complexes. For these complexes, the dissociation is catalysed by protons [2, 6] according to eqn. (2)

$$k_e = k_d + k_{H^+}[H^+] \qquad (2)$$

It is found that the constant for proton catalysis, k_H, decreases in the same sequence as do k_d values (Table II). A similar behaviour has been found previously for Li^+ and Na^+ complexes of (2, 2, 1) [5]. Assuming that the site of attack of the proton is one of the nitrogen lone pairs, conformation rigidity resulting from increased benzo group substitution should decrease k_{H^+}, as is observed. Similar, but much larger, trends were observed for K^+ and Rb^+ complexes in propylene carbonate [7]. With the larger cations, conformational changes are presumably more difficult, and more sensitive to substituent effects.

Enthalpies and Entropies of Complex Formation

The thermodynamic parameters for the complex formation of alkali metal ions with (2_B, 2_B, 2) and (2_D, 2, 2) are given in Table III. The heats of reaction, ΔH_c, like those of (2, 2, 2) and (2_B, 2, 2) determined earlier, show a similar dependence on ion-size as that of the Gibbs free energy of complexation, $\Delta G_c = -RT \ln K_s$. For K^+, Rb^+ and Cs^+, the effect of the substituents is to increase ΔH_c, exemplified by the positive differences in Fig. 2. It may be seen that ΔH_c for $Rb(2, 2, 2)^+$ is slightly more negative than that of $K(2, 2, 2)^+$, and that the values are equal for the (2_D, 2, 2) complexes. This suggests that the optimal radius for an ion with these two ligands lies between that of K^+ and Rb^+. However, the reduction in cavity size on addition of the benzo groups makes the ΔH_c values for K^+ more negative than those of the corresponding Rb^+ complexes. This reduction in cavity size increases the contact between the donor sites of the cryptand and the cation, and thus the

TABLE III. Gibbs Free Energies (ΔG_c), Enthalpies (ΔH_c) and Entropies (ΔS_c) of Cryptate Formation by Alkali Cations with Ligands (2_B, 2_B, 2) and (2_D, 2, 2) in Methanol at 25 °C.

Cry	$-\Delta G_c$[kJ/mol]		$-\Delta H_c$[kJ/mol]		$-\Delta S_c$[JK^{-1} mol^{-1}]	
	(2_B, 2_B, 2)	(2_D, 2, 2)	(2_B, 2_B, 2)	(2_D, 2, 2)	(2_B, 2_B, 2)	(2_D, 2, 2)
Li^+	<11.5	11.5				
Na^+	43.4	40.2	42.5	33.4	−3.1	−23.0
K^+	49.9	53.8	66.2	64.1	54.7	34.6
Rb^+	33.8	43.5	53.7	63.9	66.6	68.5
Cs^+	14.9	18.3	38.5	44.3	79.3	87.2

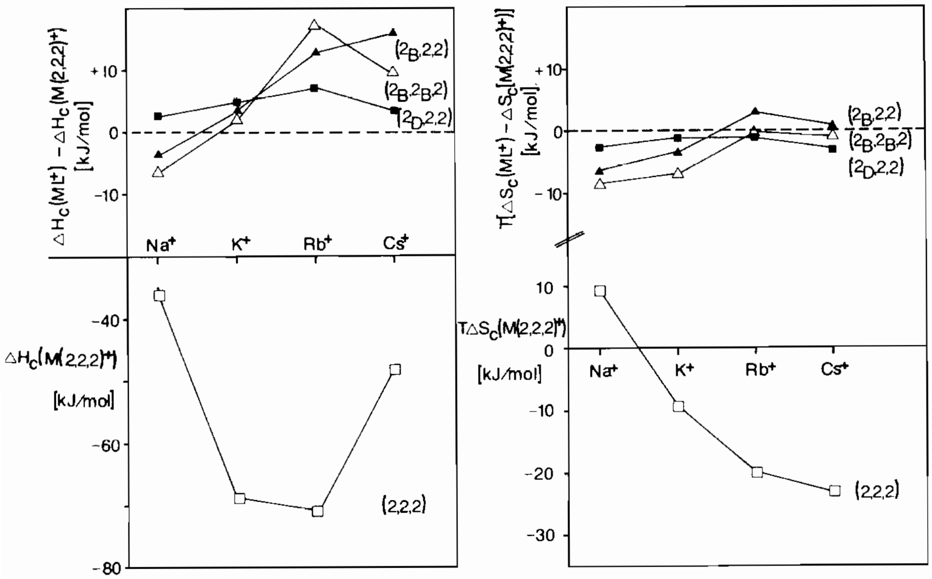


Fig. 2. Enthalpies (ΔH_c) and entropies ($T\Delta S_c$) of reaction for alkali metal cryptates with cryptand (2, 2, 2) and the effects of substituents on ΔH_c and $T\Delta S_c$, in methanol at 25 °C.

heats of reaction of Na^+ complexes become more negative in the sequence (2_D, 2, 2), (2_B, 2, 2), (2_B, 2_B, 2). In the case of the larger cations, K^+, Rb^+, and Cs^+, the increased interaction is offset by additional deformation energy required during complexation, with the net effect being an increase in ΔH_c.

The entropies of complexation, ΔS_c, are positive only for the Na^+-cryptates of (2, 2, 2) and its derivatives, and become increasingly more negative with increasing ion size for the other cations (Fig. 2). The variations in ΔS_c with substituent are clearly small compared with those for a given ligand with different cations. ΔS_c values depend both upon the changes in ligand conformation and in the solvation entropies of all reacting species. In order to eliminate this latter term for the alkali cations, the entropies of ligation, ΔS_l, for the process

$$M^+_{(g)} + L^+_{solv} \rightleftharpoons ML^+_{solv}$$

have been calculated (Table IV) using tabulated solvation entropies ΔS_{solv} [3], ($\Delta S_l = \Delta S_{solv} + \Delta S_c$). The variation of ΔS_l with cation and with the various (2, 2, 2) ligands is much smaller than that of ΔS_c, and only for Na^+ and K^+ complexes is there any systematic variation of ΔS_l with substitution.

Enthalpies and Entropies of Activation

Previous studies on the dependence of formation and dissociation rates on cation, ligand and solvent suggest that the state of the reactants in the activated complex is much more similar to that of the free species than that of the equilibrium complex [7]. A similar conclusion follows from the activation enthalpies (Table V), which show that the enthalpies of activation in the forward direction, $\Delta H^{\ddagger}_f$, are much smaller than those for the dissociation reactions, $\Delta H^{\ddagger}_d$.

TABLE IV. Solvation Entropies ΔS_{solv} of Alkali Cations and Ligation Entropies of Cryptate Formation in Methanol at 25 °C.

M^+	$-\Delta S_{solv}$ [J/mol K]	$-\Delta S_l$ [J/mol K]			
		(2, 2, 2)	(2_D, 2, 2)	(2_B, 2, 2)	(2_B, 2_B, 2)
Na^+	206	175	183	196	203
K^+	169	200	204	212	224
Rb^+	146	212	215	202	213
Cs^+	136	213	223	186	215

TABLE V. Kinetic Activation Parameters for Some Alkali Metal Cryptates in Methanol at 25 °C.

	$E_{A,f}$	$E_{A,d}$	$\Delta G_f^{\ddagger}$	$\Delta G_d^{\ddagger}$	$\Delta H_f^{\ddagger}$	$\Delta H_d^{\ddagger}$	$\Delta S_f^{\ddagger}$	$\Delta S_d^{\ddagger}$
$Na(2_D,2,2)^+$	18.7	52.1	29.5	69.8	16.2	49.6	−44.7	−67.7
$Na(2_B, 2, 2)^+$	17.8	57.6	28.0	70.5	15.3	55.0	−42.6	−52
$Na(2_B, 2_B, 2)^+$	22.3	64.7	29.1	72.5	19.7	66.2	−31.7	−34.5
$K(2_D, 2, 2)^+$	10.8	75	26.9	80.6	8.4	72.5	−62.0	−27.3
$K(2_B, 2, 2)^+$	13.9	79.3	25.0	77.6	11.4	76.7	−45.6	−3
$K(2_B, 2_B, 2)^+$	18.3	84.5	26.3	76.2	15.8	82.0	−35.2	+19.5
$Rb(2_D, 2, 2)^+$	15.7	79.7	29.5	71.5	13.2	77.3	−54.6	−19.3
$Rb(2_B, 2, 2)^+$	12.5	70.1	24.5	65.6	10.0	67.7	−48.7	+7
$Rb(2_B, 2_B, 2)^+$	18.0	71.7	27.1	61.0	15.5	69.2	−38.8	+27.8

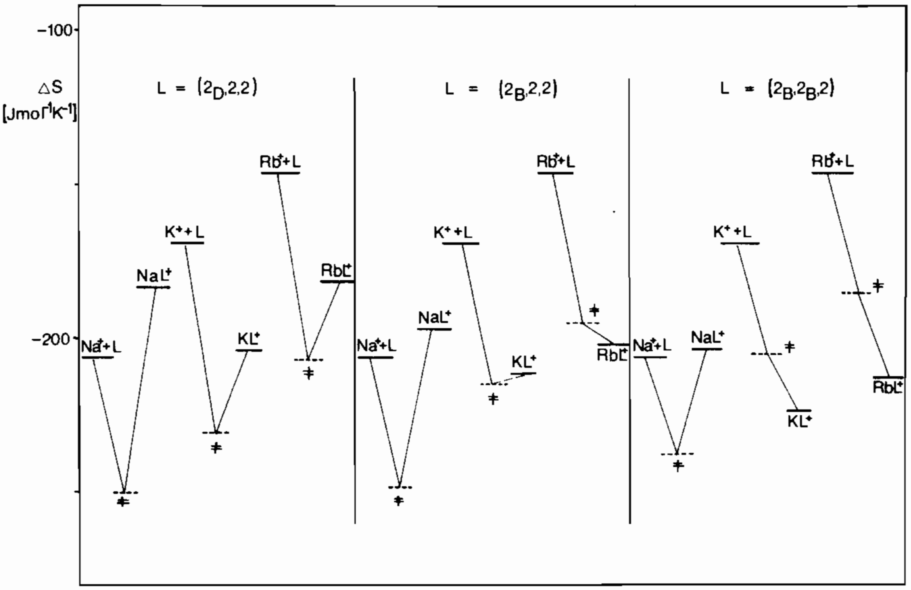


Fig. 3. Schematic reaction profile presentation for the entropies of complex formation between alkali cations and the cryptands L = (2_D, 2, 2), (2_B, 2, 2), and (2_B, 2_B, 2) in methanol at 25 °C (‡ abbreviation for activated complex).

Simple trends with both ion size and ligand substitution are much more obvious in the values for the activation entropies. The activation entropy of complex formation, $\Delta S_f^\ddagger$, is negative in all cases, because of the loss in translational and overall rotational motion [8], when the activated complex is formed.

The activation entropy for the dissociation process $\Delta S_d^\ddagger$ changes sign (Table V) depending upon the system involved. It has a large negative value for the Na^+ complexes, mainly because of the formation of an almost complete solvation shell around the departing Na^+ in the activated state. This contribution to $\Delta S_d^\ddagger$ is reduced, and in some cases overcompensated, as the cations become larger or as the cavity size decreases in the sequence $(2_D, 2, 2) > (2_B, 2, 2) > (2_B, 2_B, 2)$. In terms of these two trends, the entropie changes are characterized by (α) a shift of the entropy of the activated complex towards that of the reactants, and (β) a large shift of the product cryptate's entropy from above that of the reactants ($\Delta S_c > 0$, $\Delta S_d^\ddagger < 0$), to below that of the activated state ($\Delta S_c < 0$, $\Delta S_d^\ddagger > 0$), which is given schematically for illustration in Fig. 3. This remarkable variation in $\Delta S_d^\ddagger$ is an indication of the severe steric strain in the cryptand when the size of the cryptand is smaller than that required for an optimal fit. By contrast, since in the activated state the cation is not yet enveloped by the ligand, variations in $\Delta S_f^\ddagger$ are much smaller.

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