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New 2-Methylenepropylene-Bridged Cryptands with High Sodium Ion Selectivity: A Thermodynamic Study of Complexation

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Abstract. Thermodynamic quantities for the interactions of mono- and tri(2-methylenepropylene)-bridged cryptands, cryptand [3.3.1], cryptand [2.2.2], and 18-crown-6 with Na^+, K^+, Rb^+, and Cs^+ have been determined by calorimetric titration in an 80 : 20 (v/v) methanol : water solution at 25 °C. Incorporation of the 2-methylenepropylene (—$CH_2C(=CH_2)CH_2$—) bridge(s) into cryptand [2.2.2] results in a large change in the ligand-cation binding properties. Tri(2-methylenepropylene)-bridged cryptand [2.2.2] (**2**) shows high selectivity factors for Na^+ over K^+ and other alkali cations, while 2-methylenepropylene-bridged cryptand [2.2.2] (**1**) selects K^+ over Na^+, as does cryptand [2.2.2]. The K^+/Na^+ selectivity is reversed with increasing numbers of 2-methylenepropylene bridges. This observation indicates that increasing the number of 2-methylenepropylene bridges on cryptand [2.2.2] favors complexation of a small cation over a large one. The log K values for the formation of **1** and **2** complexes (except **1**–Cs^+ and **2**-Na^+) decrease as compared with those for the corresponding [2.2.2] complexes. Formation of six-membered chelate ring(s) by the propyleneoxy unit(s) of **1** and **2** with a cation stabilizes the cryptate complexes of the small Na^+ and destabilizes the complexes of large alkali metal cations. Thermodynamic data indicate that the stabilities of the cryptate complexes studied are dominated mostly by the enthalpy change. In most cases, both stabilization of Na^+ complexes and destabilization of the complexes of large alkali metal cations by six-membered chelate ring(s) also result from an enthalpic effect. Cryptand [3.3.1] shows a selectivity for K^+ over Cs^+, despite its two long $CH_2(CH_2OCH_2)_3CH_2$ bridges. The [3.1] macroring portion of [3.3.1] may be too small to effectively bind the Cs^+, resulting in the low stability of the Cs^+ complex.

Key words: Cryptand, alkali metal ion selectivities, equilibrium constant, enthalpy change, entropy change.

1. Introduction

Cryptands, cryptahemispherands [1], spherocryptands, and spherands (Figure 1) are excellent complexing agents for alkali and alkaline-earth cations [2, 3]. The two most important features of these ligands are their high cation-binding constants and good cation selectivities in water and in other solvents. Many of these compounds

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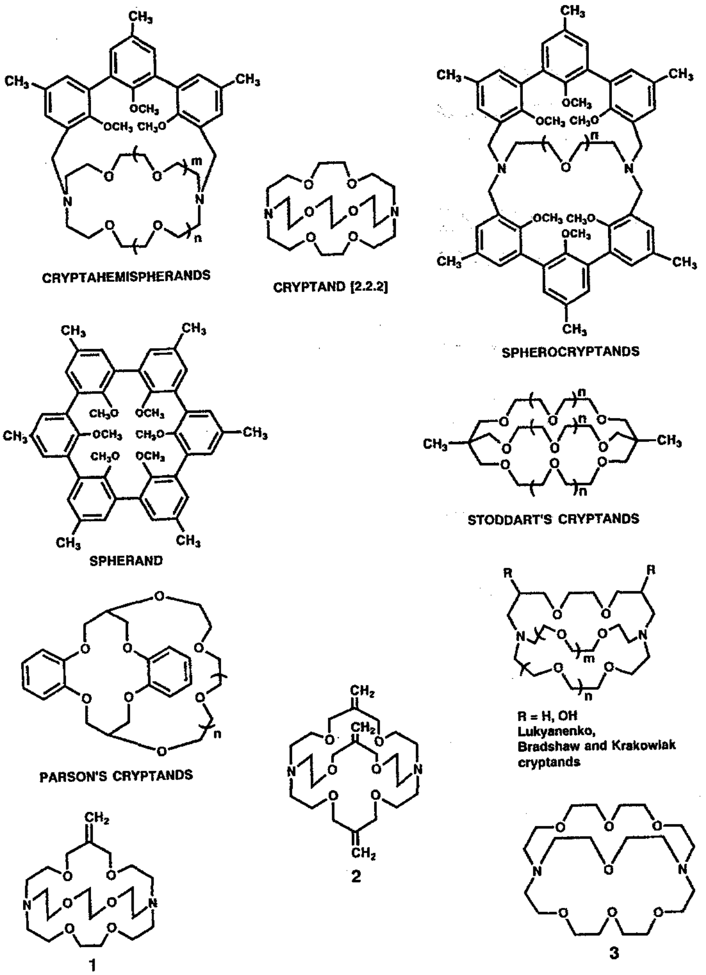

Figure 1. Structures of cryptahemispherands, spherocryptands, spherands, and cryptands.

have been synthesized and their complexation behavior with alkali and alkaline-earth metal ions has been studied [1–16].

Cryptands, such as [2.2.2], [3.2.2], and [3.3.2], which were first synthesized by Lehn and coworkers [17], consist of ethyleneoxy chains as bridges and nitrogen atoms as bridgeheads. Efforts have been made to modify the structures of these nitrogen-ethyleneoxy cryptands in order to either further enhance cation-binding ability or to study the structural influence on cryptand properties [9–16]. Some carbon-bridgehead cryptands, such as Parsons' cryptand-like molecules (Figure 1), show an enhanced cation-binding ability as compared with the nitrogen-ethyleneoxy cryptands [18]. The cryptand-like macrobicycles reported by Coxon and Stoddart, which also have two carbon bridgeheads (Figure 1), have very low complexing ability [19], probably due to an unfavorable shape of the cavity.

Macrocycle rigidity and aromatic or other substituents have an effect on cation-binding ability. A remarkable change in cation binding and selectivity was observed for the cryptahemispherands by introducing benzene rings or other rigid substituents [20]. For highly rigid molecules, the most important factor for proper complexing is the size of the cavity and the number of complexing heteroatoms, as can be seen for the spherands. Only a few of the spherands which have the proper sized cavity are good complexing agents with high selectivity [21, 22].

Cryptands and monocyclic crown ethers containing both ethyleneoxy and propyleneoxy units have different complexing properties from all-ethyleneoxy-containing cryptands and crown ethers [14–16, 23–26]. Replacement of one or several ethyleneoxy by propyleneoxy units in a macrocyclic ligand favors complexation and selectivity of small alkali cations (Li^+ and Na^+) by small crown ethers of the crown-4 and crown-5 types but decreases complex stability for large cations with large-sized crown ethers [23–26]. Such replacements usually decrease cation-binding strengths and cation selectivities of the cryptands [14–16]. Lukyanenko and coworkers studied cryptands containing two propylene bridges [14]. Only a few of these cryptands demonstrated higher stability constants in 95 : 5 (v/v) methanol : water solvent (95% MeOH) than the corresponding cryptands containing only ethylene bridges. We have also shown that cryptands containing two propylene bridges form much weaker complexes with Group IA and IIA cations than the corresponding cryptands with only ethylene bridges [15]. A bis(2-methylenepropylene)-bridged cryptand [2.2.2] was shown to have no K^+/Na^+ selectivity [16]. We herein report thermodynamic quantities determined for interactions of cryptands having one and three 2-methylenepropylene bridges and of two all-ethylene-bridged cryptands, [3.3.1] and [2.2.2], with Na^+, K^+, Rb^+, and Cs^+ in an 80 : 20 (v/v) methanol : water (80% MeOH) solution.

2. Experimental

2.1. MATERIALS

Cryptands **1–3** (Figure 1) were synthesized according to procedures published earlier [12]. Cryptand [2.2.2] and 18-crown-6 (18C6) were obtained from Aldrich Chemical Company. $NaNO_3$ (Aldrich), KNO_3 (Mallinckrodt AR), $RbNO_3$ (Aldrich), CsI (Aldrich), and methanol (Fisher, HPLC grade) were used as purchased. CsI was used because of the low solubility of $CsNO_3$ in 80% MeOH. $CsNO_3$ (Johnson Matthey) was also used in several calorimetric runs (more than 100 data points had to be taken due to the low salt concentration) in order to confirm the results obtained by using CsI. Little difference in 80% MeOH solvent was found using the two different cesium salts. The purity of all inorganic salts used was greater than 99.9%.

2.2. DETERMINATION OF THERMODYNAMIC QUANTITIES

Equilibrium constant (K) and enthalpy change (ΔH) values for the interaction of the alkali metal ions with the macrocyclic ligands were determined calorimetrically in 80% MeOH solution at 25.0 ± 0.1 °C using a Tronac 450 isoperibol titration calorimeter. The corresponding entropy change (ΔS) values were calculated according to the relation $RT \ln K = \Delta H - T\Delta S$. The initial solution volume in the Dewar was 20 mL. The calorimeter was calibrated as reported [27]. Concentrations of metal ion solutions were 8×10^{-2} to 0.12 M (5×10^{-2} M for $CsNO_3$) and those of macrocyclic ligands were 2×10^{-3} to 4×10^{-3} M. The metal ion solutions were titrated into the cryptand or crown ether solutions. The titration experiments showed that all host–guest interactions studied had a 1 : 1 cation-ligand ratio. For interactions having log K values larger than 5.5, the values were determined by a competitive titration procedure [28].

3. Results and Discussion

3.1. EFFECT OF REPLACEMENT OF ETHYLENE GROUP(S) BY METHYLENEPROPYLENE GROUP(S)

Log K, ΔH, and $T\Delta S$ values for the interactions studied are listed in Table I. Incorporation of 2-methylenepropylene group(s) into cryptand [2.2.2] results in a large change in cation-binding properties. Ligand **1** forms less stable complexes with most cations studied as compared with cryptand [2.2.2] (Table I). Selectivity behavior of **1** is similar to that of [2.2.2] (see Figure 2). On the other hand, the complexation behavior of **2** is very different from that of [2.2.2], as is illustrated in Figure 2. Ligand **1** differs from cryptand [2.2.2] in that one CH_2CH_2 group is replaced by a 2-methylenepropylene $CH_2C(=CH_2)CH_2$ group. The planarity of $CH_2C(=CH_2)CH_2$ could change the cryptand conformation and result in a change in cation-binding properties (see discussion below). It was expected that the cryptand cavity would be enlarged by incorporating the methylenepropylene unit(s) into the molecule since $CH_2C(=CH_2)CH_2$ is longer than the CH_2CH_2 group and the resulting ligand(s) should selectively bind a large cation. But actual complexation behavior is not as simple as expected. Compound **1** forms the most stable complex with K^+, as is seen with cryptand [2.2.2]. Complexes of **1** with Na^+, K^+, and Rb^+, but not Cs^+, are destabilized by introducing the methylenepropylene bridge as compared with cryptand [2.2.2]. When three methylenepropylene groups are incorporated into cryptand [2.2.2] to form **2**, two effects are seen. First, **2** binds the small Na^+ more strongly than any of the other cations. The stability order $Na^+ \gg K^+ > Rb^+ > Cs^+$ is quite different from that of either cryptand [2.2.2] or **1**, as is seen in Figure 2. Second, the stability of the Na^+ complex with **2** is higher than that of the Na^+ complex with either the single-bridged **1** or cryptand [2.2.2].

Different numbers of methylenepropylene bridges result in changes in selectivity. Single-bridged **1** selects K^+ over Na^+ like cryptand [2.2.2]. The double-bridged

Table I. Log K, ΔH (kJ/mol), and $T\Delta S$ (kJ/mol) values[a] for interactions of several cryptands and 18-crown-6 with alkali metal ions in an 80 : 20 (v/v) methanol : water solution at 25.0 °C

Ligand	Metal ion	log K	ΔH	$T\Delta S$
1	Na^+	5.60 ± 0.10	-46.3 ± 0.3	−14.3
	K^+	7.08^b	-54.1^b	−13.7
	Rb^+	5.70^b	-51.0^b	−18.5
	Cs^+	2.96 ± 0.03	-48.9 ± 2.7	−32.0
2	Na^+	6.50 ± 0.07	-71.7 ± 0.8	−34.6
	K^+	3.60 ± 0.02	-43.5 ± 0.4	−23.0
	Rb^+	2.49 ± 0.03	-24.2 ± 0.3	−10.0
	Cs^+	$<2^c$	c	
3	K^+	3.99^b	-32.8^b	−10.0
	Cs^+	2.04^b	-51.8^b	−40.4
[2.2.2]	Na^+	6.04 ± 0.18	-40.5 ± 1.5	−6.0
	K^+	8.52 ± 0.19	-65.8 ± 2.1	−17.2
	Rb^+	7.10 ± 0.22	-59.6 ± 2.2	−19.1
	Cs^+	2.84 ± 0.06	-29.7 ± 0.2	−13.5
18C6	Na^+	3.05 ± 0.01	-23.3 ± 0.5	−5.9
	K^+	4.70 ± 0.02	-45.3 ± 0.2	−18.5
	Rb^+	3.99 ± 0.03	-36.6 ± 0.4	−13.8
	Cs^+	3.40 ± 0.03	-27.7 ± 0.8	−8.3

[a] Log K values larger than 5.5 were determined by a competitive calorimetric titration.
[b] Only one run was possible due to limited quantity of the ligand.
[c] Both direct and competitive (with K^+) titrations show small log K and ΔH values.

cryptand (not shown in this paper) forms Na^+ and K^+ complexes with almost the same stability [16] (log K values in 80 : 20 (v/v) $CD_3OD : D_2O$ solvent: 4.0 ± 0.3 for Na^+ and 3.8 ± 0.2 for K^+). With three methylenepropylene chains, cryptand **2** selects Na^+ over K^+ with a large selectivity factor ($K_{Na^+}/K_{K^+} = 790$). In fact, **2** shows a high selectivity for Na^+ over all other alkali metal ions studied (Table I and Figure 2). Thus, the more methylenepropylene bridges a cryptand [2.2.2] has, the more strongly the cryptand binds a small cation.

High selectivity for the small cation by **2** could be caused by six-membered chelate rings. All-ethylene-containing cryptate complexes have only five-membered chelate rings but incorporation of the propylene bridges into cryptand [2.2.2] results in the cryptate complexes containing several six-membered chelate rings. From an examination of binding-constant data and molecular mechanics calculations, Hancock has concluded that large metal ions prefer five-membered chelate rings while small metal ions have a high preference for six-membered chelate rings [29, 30]. Therefore, increasing the number of six-

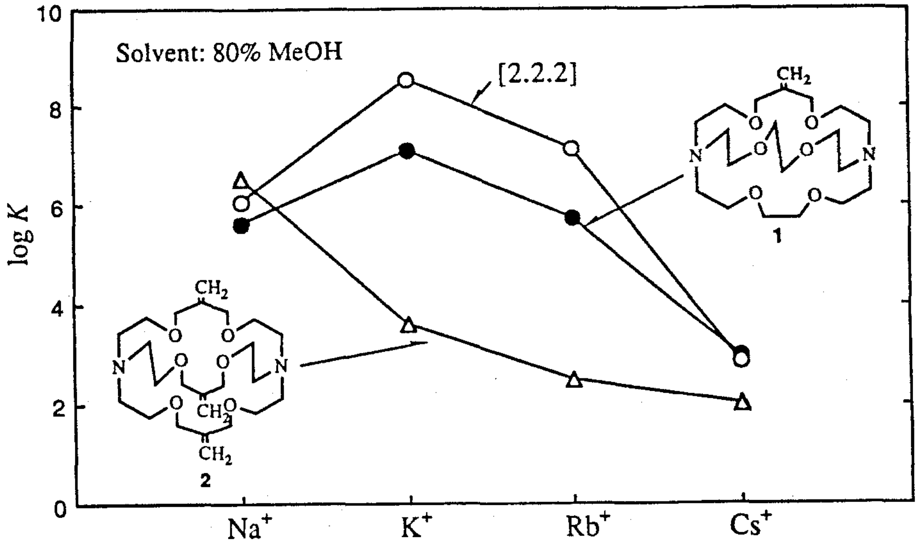

Figure 2. Plots of log *K* vs. the alkali cations for their interactions with cryptand [2.2.2] and 2-methylenepropylene-bridged cryptands (**1** and **2**).

membered chelate rings from one in complexes of **1** to three in complexes of **2** favors complexation of small-sized Na^+ over larger cations. A similar situation has been observed by Lukyanenko and coworkers [14]. As two 2-hydroxypropylene groups are incorporated into cryptand [2.2.2], the resulting ligand selects Na^+ ($\log K = 5.75$ in 95% MeOH) over K^+ ($\log K = 5.13$ in 95% MeOH). The substituents on the propylene chain also have an important effect on cation binding. If two unsubstituted propylene units are introduced into cryptand [2.2.2], the ligand still selects K^+ over Na^+ [14]. It is, therefore, the hydroxy groups on the propylene units that cause the cryptand to select Na^+ over K^+. Thus, the methylene double bond on the propylene bridges must play an important role in the reversed Na^+/K^+ selectivity.

The double bonds attached to the propylene units result in a planar structure of the $CH_2C(=CH_2)CH_2$ group that may cause a conformational change in **2** so that this ligand binds Na^+ much stronger than K^+. The higher binding constant for Na^+ over K^+ by the bis(2-hydroxypropylene)-bridged cryptand [2.2.2] was attributed to a structural change of the ligand [14]. Truter and coworkers noted that different isomers of a cryptand resulting only from different configurations of two cyclohexane rings had very different cation-binding abilities [31]. The difference in stability constants (in methanol at 25 °C) for Rb^+ was as large as $10^{4.7}$. For Na^+ and K^+, the differences were $10^{3.7}$ and $10^{3.5}$, respectively [31]. Thus, it is possible in our case for the planar rigid $CH_2C(=CH_2)CH_2$ group to deform the cryptand cavity so that a large change in cation binding occurs. CPK molecular models show a different conformation of **2** from that of a compound having C—C single bonds in the place of double bonds of **2** and a remarkably different shape of the cavity of **2** from that of the cavity of cryptand [2.2.2]. In addition, the increase in the molecular rigidity by introducing double bonds favors Na^+ complexation. Therefore, two factors, three six-membered chelate rings and three double bonds, are probably responsible for the selective binding of small Na^+ to **2**.

3.2. ENTHALPIC AND ENTROPIC EFFECTS OF CRYPTAND COMPLEXATION

Thermodynamic data indicate that formation of all cryptand complexes studied is enthalpy driven. Entropy changes are unfavorable in all cases. It can be seen from Table I that enthalpy changes are responsible for the high stabilities of the cryptate complexes. The increased log K value for formation of the Na^+–**2** complex as compared with the Na^+–**1** complex is a result of a large enthalpic gain. Similarly, the decrease in log K values for the interaction of **2** with K^+, Rb^+, and Cs^+ as compared with those for the interaction of **1** with these cations is mostly due to the less favorable ΔH values.

In most cases, both stabilization of Na^+ complexes and destabilization of the complexes of large cations by six-membered chelate ring(s) result from an enthalpic effect. The enthalpy change values for Rb^+ interaction with both **1** and **2** are less negative than that for Rb^+–[2.2.2] interaction while the $T\Delta S$ values for both Rb^+–**1** and Rb^+–**2** interactions are less unfavorable than that for the Rb^+–[2.2.2] interaction, indicating that destabilization of Rb^+ complexes by introducing a six-membered chelate ring in **1** and three such rings in **2** is a result of decreased enthalpic gains. On the other hand, stabilization of the Na^+– **2** complex by three six-membered chelate rings is due to a larger enthalpic gain (−71.7 kJ/mol) as compared with Na^+–[2.2.2] complexation which shows a smaller $-\Delta H$ value (−40.5 kJ/mol). The entropy change for Na^+–**2** interaction is more negative than that for Na^+–[2.2.2] complexation. This observation supports the enthalpy–entropy compensation principle described by Inoue and coworkers [32]. Compared with [2.2.2], however, decreased stability for the K^+–**1** complex by a six-membered chelate ring is attributed to the enthalpic effect but that for the K^+–**2** complex by three six-membered chelate rings results from both enthalpic and entropic effects.

3.3. CRYPTAND [3.3.1] AND MONOCYCLIC 18C6

The K^+ complex of cryptand [2.2.2] is more stable than those of any other alkali metal ions [33]. This selectivity has long been understood to be due to the size match between the ligand cavity and the radius of K^+ [33, 34]. From the size-match point of view it is expected that a ligand with a cavity size larger than [2.2.2] should exhibit selectivity toward cations larger than K^+. Hence selectivity for Rb^+ and Cs^+ is expected as the cavity size increases. However, data in Table I show that cryptand [3.3.1] (**3**) still selects K^+ over Cs^+ in spite of its two long $CH_2(CH_2OCH_2)_3CH_2$ bridges. This result indicates that the [3.1] macroring

Table II. Stability constants for K^+ and Cs^+ interactions with several cryptands at 25 °C.[a]

Cryptand	Cation	log K	Solvent	Selectivity factor[b]
[2.2.2]	K^+	9.75	95% MeOH	
	Cs^+	3.54	95% MeOH	$K^+/Cs^+ = 10^{6.21}$
[3.3.1]	K^+	3.99	80% MeOH	
	Cs^+	2.04	80% MeOH	$K^+/Cs^+ = 89$
[3.2.2]	K^+	2.2	water	
	Cs^+	2.0	water	$K^+/Cs^+ = 1.6$
[3.3.2]	K^+	6.0	MeOH	
	Cs^+	>6.0	MeOH	$Cs^+/K^+ > 1$
[3.3.3]	K^+	5.4	MeOH	
	Cs^+	5.9	MeOH	$Cs^+/K^+ = 3.2$

[a] Except for [3.3.1], the data are from Ref. 32.

[b] The ratio of stability constants of K^+ to Cs^+ or Cs^+ to K^+.

portion is still too small to accommodate Cs^+. With increasing cavity size from [3.3.1] through [3.2.2] and [3.3.2] to [3.3.3], K^+/Cs^+ selectivity decreases and Cs^+/K^+ selectivity increases. Cryptand [3.3.3] shows selectivity for Cs^+ over K^+ by a factor of 3.2 (Table II). Therefore, in order to select a large cation, the cryptand should not be designed to have a short chain that may deform the cavity.

The stabilities of complexes of **2** with large cations (K^+, Rb^+, and Cs^+) are lower than those of corresponding monocyclic 18C6 complexes (Table I), demonstrating again that six-membered chelate rings destabilize the complexes of large-sized cations. All cryptate complexes with Cs^+ are also less stable than 18C6–Cs^+ complexes. The observation indicates that the three-dimensional cryptands may bind cations more weakly than the planar crown ethers if the sizes of the cryptand cavity and the cation do not match each other.

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