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Complexation Properties of a Carbon-Bridged Cryptand with Metal Ions in Aqueous Solution at 25°C

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Thermodynamic quantities (log K, ΔH, and ΔS) for the interactions of a carbon-bridged cryptand with Li^+, Na^+, K^+, Ca^{2+}, Sr^{2+}, Ba^{2+}, and Pb^{2+} were determined at 25° C by calorimetric titration in aqueous solution. The cryptand forms complexes with Na^+, Sr^{2+}, Ba^{2+}, and Pb^{2+} with log $K \geq 2$. Complexation was not detected for Li^+, K^+, and Ca^{2+}. Weak interactions with Li^+ and K^+ and a log K value of 2.4 for Na^+ suggest that the cavity size of the cryptand is close to that of Na^+ but too small for K^+ and too large for Li^+. The carbon-bridged cryptand selectively binds Sr^{2+} (log $K = 3.2$) over Ca^{2+} and Ba^{2+} by more than one order of magnitude.

Keywords: Carbon-bridged cryptand; Complexation; Calorimetric titration

INTRODUCTION

The alkali and alkaline earth metal ions have greater interaction with hard oxygen donor atoms than with soft sulfur atoms. Trivalent nitrogen donor atoms allow the synthesis of cryptands, supercryptands, and other complicated and rigid structures [1]. The cryptands, prepared more than 30 years ago, exhibit very strong interactions with a variety of metal cations, particularly under basic conditions [2, 3]. There is a great need for three-dimensional ligands capable of binding the alkali and alkaline earth metal ions in both acidic and basic media. Thus, it is important to prepare new bicyclic ligating compounds which do not contain nitrogen functions and to study their affinities for metal ions.

A number of rigid non-nitrogen-containing ligands have been investigated. The spherands, prepared by Cram and co-workers [4, 5], and carbon-bridged cryptands (CB cryptands) have excellent complexation properties toward the alkali and alkaline earth metal ions. The first CB cryptands, prepared by Coxon and Stoddard (**SCB** see Fig. 1) [6, 7], had poor affinities for the alkali metal ions possibly due to an unfavorable shape of the cavity. In the **SCB** ligands, three

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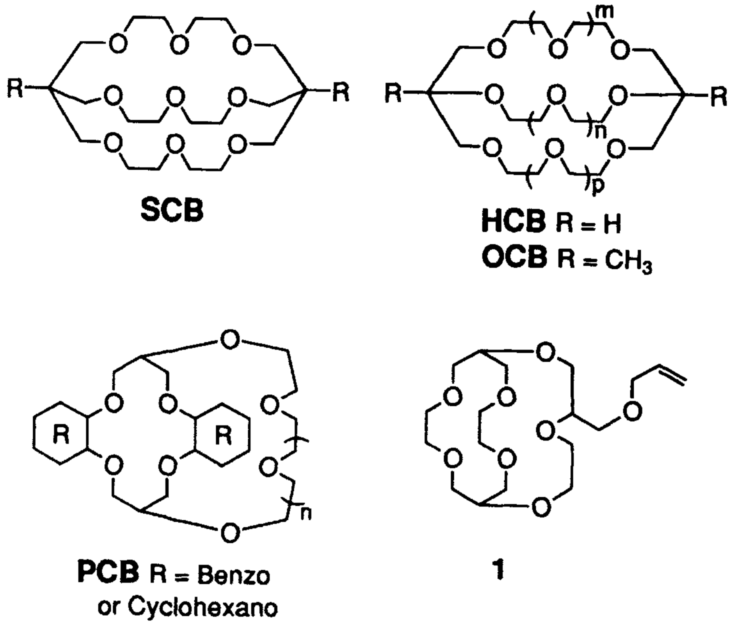


SCB

HCB R = H
OCB R = CH_3

PCB R = Benzo
or Cyclohexano

1

FIGURE 1 Carbon-bridged cryptands.

diethyleneoxy chains are linked through propylene bridge units on each end. Haines and co-workers [8,9] found that CB cryptands connected through ethylene and propylene bridges (**HCB**) had improved affinities toward K^+. In this case, one of the oligoethylene chains of **HCB** had one less methylene group on each end than did the **SCB** cryptands. The Haines group prepared large cavity CB cryptands containing 3:4:4 oxygen atoms ($m = 1, n = p = 2$) and 4:4:4 oxygen atoms ($m = n = p = 2$) but did not study their metal ion complexing abilities [8,9]. Similar CB cryptands, when bound to inorganic supports, are useful for removing and concentrating lead, thalium, and the alkali and alkaline earth metal ions from concentrated aqueous solutions [10].

Parsons and co-workers [11–13] prepared a series of dibenzo and dicyclohexano-containing CB cryptands (**PCB**) based on the dibenzo-14-crown-4 structure. These somewhat more rigid CB cryptands exhibited the high affinity for alkali metal ions which is observed for the nitrogen-bridged cryptands but with a diminished selectivity. The **PCB** cryptands contained 2:2:3 ($n = 0$), 2:2:4 ($n = 1$), and 2:2:5 ($n = 2$) oxygen atoms. Okahara and co-workers [14] prepared a series of CB cryptands (**OCB**) like those of Haines and Karntiang [9] except that the **OCB** cryptands contained a methyl substituent on each of the two bridgehead carbon atoms. The Okahara group found that the **OCB** cryptands had lower affinities for Na^+ and K^+ in methanol than the corresponding nitrogen-bridged cryptands, but they formed stronger complexes with Na^+ and K^+ than did the less rigid crown ethers.

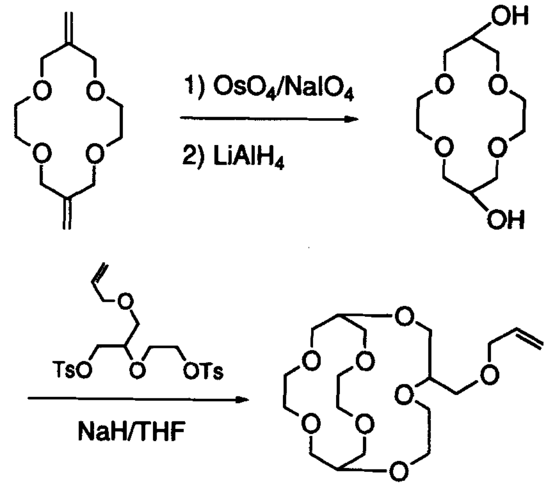
The metal ion complexing properties of the nitrogen-bridged cryptands have been studied extensively [3] because their ease of preparation make them readily available. The CB cryptands have been prepared by only four synthetic groups because they are difficult to prepare. Only recently have two of the CB cryptands with methyl substituents become available [15].

This work concerns metal ion complexation properties of CB cryptand [3.2.2] (**1**), which contains 2:2:3 oxygens. This nomenclature is similar to that of the nitrogen-bridged cryptands in that the numbers refer to the numbers of oxygen atoms in chains connecting the two carbon-atom bridgeheads. The calorimetric study indicates that **1** exhibits good selectivity not only for Na^+ over Li^+ and K^+ but also for Sr^{2+} over other metal ions studied.

RESULTS AND DISCUSSION

Synthesis of CB Cryptands

There are only two synthetically useful methods to prepare CB cryptands. The first one, reported by Okahara and co-workers [14], uses the reaction of di(bromomethyl)crown ethers with the appropriate oligoethylene glycol. More recently, we have used the reaction of a dihydroxycrown ether with a ditosylate to form the CB cryptands [10, 16] as shown in Scheme 1. This method allows the preparation of CB cryptands with methyl groups at the two bridgehead carbon atoms [16] or with hydrogen atoms as in **1** [10]. The first step is the preparation of the 6,13-dimethylene-1,4,8,11-tetraoxacyclotetradecane [17] followed by oxidation and reduction steps to form the dihydroxy-14-crown-4 [10, 16, 18]. Reaction of the dimethylene-containing crown ether with mercuric acetate followed by reduction with sodium borohydride and hydrolysis gave the dihydroxy-dimethyl-substituted crown ether needed to prepare the **OCB** ligands [16]. The non-dimethyl-substituted crown ether diols were prepared as shown in Scheme 1 [10]. The dihydroxycrown ether was then treated with sodium hydride followed by allyloxymethyl-substituted triethylene glycol ditosylate [19, 20] to give **1** (Scheme 1). This new method [10, 15] allows the preparation of the CB cryptands by a shorter pathway and in good overall yields.



1

SCHEME 1 Preparation of **1**.

Complexation and Selectivity for Cations by 1

The results of an evaluation of the thermodynamic parameters for the interactions of **1** with Li^+, Na^+, K^+, Ca^{2+}, Sr^{2+}, Ba^{2+}, and Pb^{2+} are listed in Table I. The log *K*, ΔH, and $T\Delta S$ values are the averages taken from two to four determinations. Uncertainties in the table are given as standard deviations. In aqueous solution, **1** forms complexes with Na^+, Sr^{2+}, Ba^{2+}, and Pb^{2+}. Log *K* values are close to or higher than 2. On the other hand, the interactions of Li^+, K^+, and Ca^{2+} with **1** cannot be detected calorimetrically because of very small heat effects. These results suggest that the cavity size of the cryptand is close to that of Na^+ but too small for K^+ and too large for Li^+. Pb^{2+} forms a complex with **1** with the same stability as that with Na^+.

Among the alkali metal ions, **1** selectively binds Na^+ over Li^+ and K^+. Since the log *K* values can not be calculated from calorimetric data for the Li^+ and K^+ interactions in aqueous solution, the degree of the selectivity is not known. As has been reported [21], the stabilities of cryptand complexes depend strongly on the match of the cation size and the cryptand cavity diameter. Therefore, the cavity size of **1** must match the diameter of Na^+. We expect that **1** would have a weak ability to complex the two

TABLE I Log *K*, ΔH, and $T\Delta S$ values for interactions of CB cryptand **1** with metal ions in aqueous solution at 25.0° C (log *K* values for reported cryptands in water or methanol are listed for comparison)

Ligand	Metal ion	log *K*	ΔH (kj/mol)	$T\Delta S$ (kj/mol)
1	Li^+	[a]		
	Na^+	2.39 ± 0.07	-6.5 ± 0.2	7.1
	K^+	[a]		
	Ca^{2+}	[a]		
	Sr^{2+}	3.20 ± 0.06	-5.4 ± 0.2	12.9
	Ba^{2+}	1.93 ± 0.04	-17.3 ± 0.5	-6.3
	Pb^{2+}	2.42 ± 0.05	-8.3 ± 0.3	5.5
PCB[b]	Na^+	$5.3 \sim 5.7$		
	K^+	$5.7 \sim 5.8$		
SCB[c]	Na^+	1.1		
	K^+	2.2		
OCB1[d]	Na^+	4.33		
	K^+	7.06		
OCB2[d]	Na^+	4.26		
	K^+	2.66		

[a] No measurable heat other than heat of dilution indicates small ΔH and/or log *K* values.

[b] From Ref. 11. Log *K* values valid in water containing a trace amount of methylene chloride for the **PCB** cryptand where $n = 1$ (Fig. 1).

[c] From Ref. 7. Log *K* values valid in MeOH for the **SCB** cryptand where $R = Me$ (Fig. 1).

[d] From Ref. 14. Log *K* values valid in MeOH for **OCB1** ($n = 2, m = 1, p = 1$) and **OCB2** ($n = 1, m = 0, p = 1$) (Fig. 1).

large alkali cations Rb^+ and Cs^+. As shown in Table I, similar sized CB cryptands **SCB** and **OCB1** exhibit K^+/Na^+ selectivity. One of the Parson cryptands (PCB) forms highly stable complexes with Na^+ and K^+ but exhibits almost no selectivity between them.

Similar selectivity situations are observed for the alkaline earth metal ions. Cryptand **1** selectively binds Sr^{2+} over Ca^{2+} and Ba^{2+}. We expect that **1** would interact very weakly with small Mg^{2+}. The radius of Sr^{2+} (1.13 Å) is close to that of Na^+ (0.97 Å) and Sr^{2+} forms the most stable complex with **1** among the alkaline earth cations.

Although the size of Ca^{2+} ($r = 0.99$ Å) is the same as that of Na^+, the high hydration energy of Ca^{2+} may result in two possibilities for Ca^{2+} interaction with **1**. First, **1** is unable to desolvate the cation resulting in a very weak interaction. Second, complexation occurs but the desolvation consumes most of the binding energy. As a result, no temperature change can be detected during the titration. The second possibility is supported by the results in Table I where it is seen that the $-\Delta H$ values for M^{2+} –**1** interaction decrease from Ba^{2+} –**1** (−17.3 kj/mol) to Sr^{2+} –**1** (−5.4 kj/mol). Extrapolation to Ca^{2+} –**1** interaction suggests a near zero ΔH value.

Enthalpic and Entropic Effects of Complexation

In general, small $-\Delta H$ values for the interactions of **1** with the metal ions studied are observed in aqueous solution (Tab. I). The largest $-\Delta H$ value is observed for the complex with Ba^{2+} and this interaction gives a negative ΔS value. All of the other detected interactions have positive ΔS values, indicating that both enthalpy and entropy changes contribute to the formation of the complexes. As compared with Na^+, Ba^{2+}, and Pb^{2+}, the Sr^{2+} –**1** interaction exhibits the smallest $-\Delta H$ value (−5.4 kJ/mol) but the largest $T\Delta S$ value (12.9 kJ/mol).

Therefore, the high selectivity of **1** for Sr^{2+} originates from a favorable entropic effect, indicating that complexation of **1** with Sr^{2+} results in not only extensive desolvation but probably a small comformation change in the ligand.

EXPERIMENTAL

Materials

Reagent grade chemicals were obtained from the indicated sources and used without further purification: LiCl (Fisher), NaCl (Aldrich), KCl (Aldrich), $CaCl_2 \cdot 2H_2O$ (Aldrich), $SrCl_2 \cdot H_2O$ (Mallinckrodt), $BaCl_2 \cdot 2H_2O$ (Allied), and $Pb(NO_3)_2$ (Mallinckrodt).

Synthesis of CB Cryptand 1

The dihydroxy-14-crown-4 [18] and 2-allyloxymethyl-3-oxapentan-1,5-diol ditosylate [19,20] were prepared as described. A mixture of dihydroxy-14-crown-4 (2.82 g, 12 mmol) and sodium hydride (95% 1.35 g, 53.4 mmol) in 150 mL of THF was stirred at room temperature for 2 h and 6.00 g (12.38 mmol) of 2-allyloxymethyl-3-oxapentan-1,5-diol ditosylate in 100 mL of THF was added dropwise. The reaction mixture was stirred at room temperature for 24 h, refluxed for 48 h and evaporated under reduced pressure. The residue was triturated between chloroform and water. The organic layer was washed with water twice, dried, and concentrated. The residue was subjected to column chromatography on silica gel (methanol/ammonium hydroxide 20:1 and 10:1) to give **1** (0.52 g, 13%) as an oil; ^1H NMR ($CDCl_3$): δ 5.88 (m, 1H), 5.20 (m, 2H), 3.2–3.9 (m, 31H); MS: 376. Anal. Calcd for $C_{18}H_{32}O_8$: C, 57.43; H, 8.57. Found: C, 57.70; H, 8.19.

Determination of K, ΔH and TΔS

Equilibrium constant (K) and enthalpy change (ΔH) values for the interaction of the metal ions with **1** were determined calorimetrically in aqueous solutions at 25.0 ± 0.1° C using a Tronac 450 isoperibol titration calorimeter [22]. 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. Concentration of metal ion solutions were 0.10 to 0.15 M and those of **1** were 2.5×10^{-3} to 5×10^{-3} M. The metal ion solutions were titrated into the cryptand solution and titrations were carried out to a 2-fold excess of the metal ions. The titration experiments showed that all host-guest interactions studied had 1:1 cation:ligand ratios.

The ΔH and $T\Delta S$ values are valid at the specified experimental conditions. No inert electrolyte was used to fix the ionic strength. The reactions were carried out at low ionic strength and are isocoulombic in nature [23]. The resulting thermodynamic values are close to the standard state values valid at infinite dilution.

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