# Complexation Thermodynamics of Crown Ethers. 6.[1,2] Calorimetric Titration of Cation Complexation with Some Azacrown Ethers

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Complex stability constants ($K_s$) and thermodynamic parameters ($\Delta H°$ and $\Delta S°$) were determined in methanol at 25 °C for the stoichiometric 1:1 complexation of some alkali metal ions ($Na^+$, $K^+$, and $Cs^+$) with *N*-phenylaza-15-crown-5 (**1**), *N*-octylaza-15-crown-5 (**2**), and *N*-benzylaza-15-crown-5 to *N*-benzylaza-24-crown-8 (**3**−**6**). The *N*-substituent was shown to have a drastic effect upon complex stability of the aza-15-crown-5 series (**1**−**3**). The aza-15-crown-5 **2** possessing the least-bulky substituent afforded the most stable complexes with all cations examined and the highest $Na^+/K^+$ selectivity up to 13. The larger-sized azacrown ethers **4**−**6** gave the highest complex stabilities for the size-matched cations; i.e., **4** showed the highest $K^+/Cs^+$ selectivity up to 40, while **6** showed the highest $Cs^+/K^+$ selectivity of 10. These results indicate that the *N*-substituent plays crucial roles in addition to the size-fit concept in the complexation of azacrown ethers with a nondonating side-chain. Thermodynamically, the complexation of alkali metal ions with azacrown ethers is enthalpy-driven, but the cation selectivity is mostly entropy-governed in methanol.

## Introduction

Since the first synthesis of crown ethers with side-chain(s) attached through a carbon- or nitrogen-pivot, thermodynamic studies on the complexation of lariat ethers with cations were performed in order to elucidate the nature of the cation-binding behavior from a thermodynamic point of view and also to gain insight into the factors governing cation−ligand complexation phenomena.[3−7] Lariat ethers with additional binding sites in the side-chain(s) are known to give significantly enhanced cation-binding ability and selectivity as compared with the parent crown ether.[8−15]

We have shown that the introduction of both nondonating alkyl[16] and donating oxyethylene group(s)[17] to the carbon-pivot 16-crown-5 alter not only the cation-binding constant but also the relative cation selectivity significantly. More recently, we have demonstrated that the carbon-pivot lariats are less flexible in adjusting their conformations upon complexation than the corresponding nitrogen-pivot lariats.[2,18] The relevant thermodynamic quantities clearly indicate that the binding ability and selectivity of lariat ethers are governed by the ligand's cavity size, the type and number of additional donor atom(s) in the side-chain, and the pivot atom. However, less attention has been paid to the complexation thermodynamics of azacrown ethers with nondonating side-chain(s). In particular, the influence of substitution and ring size on the cation-binding ability/selectivity of azacrown ethers has not been investigated systematically from a thermodynamic point of view, despite the potential importance of such studies in discussing the complexation behavior of lariat ethers.

In the present study, we report our results of a thermodynamic study on the complexation of alkali metal ions ($Na^+$, $K^+$, and $Cs^+$) with *N*-phenyl-aza-15-crown-5 (**1**), *N*-octylaza-15-crown-5 (**2**), and *N*-benzylaza-15-crown-5 (**3**), *N*-benzylaza-18-crown-6 (**4**), *N*-benzylaza-21-crown-7 (**5**), and *N*-benzylaza-24-crown-8 (**6**) (Chart 1) in methanol at 25 °C. In this study, we discuss the

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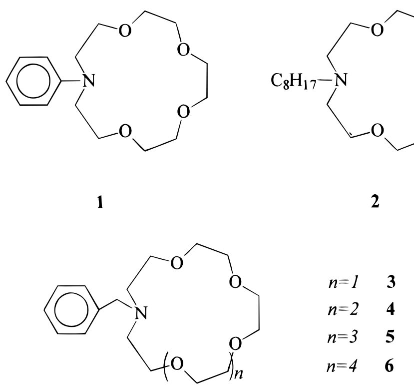
**Chart 1**



influence of the substitution and ring size upon complexation of azacrown ethers with cations from the thermodynamic point of view. The thermodynamic quantities obtained will provide further understanding of the complexation behavior of azacrown ethers with a nondonating side-chain.

## Experimental Section

**Materials.** Azacrown ethers **1**−**6** were prepared according to the procedures reported previously.[18−20] Reagent-grade methanol was refluxed over magnesium turnings and then distilled fractionally to give dry methanol for calorimetry. Analytical grade sodium chloride, potassium thiocyanate, and cesium chloride were used as received. All metal salts were dried in vacuo prior to use. The ligands **1**−**6** were dissolved in the purified methanol to make a titrate solution of 3.0−6.0 mM concentration, while the alkali metal salts were dissolved in the same solvent to make a titrant solution in 0.12−0.15 M concentration.

**Apparatus and Procedures.** Calorimetric titrations were performed at the atmospheric pressure in a temperature-controlled water bath maintained at 25.0 °C by using an LKB-8721-2 precision titration calorimeter connected to a personal computer for automated titration and data processing.[1] The principle of measurement and the detailed experimental procedures were reported elsewhere.[21,22] In a typical run, a solution of alkali metal salt (0.12−0.15 M) was continuously introduced at a rate of 0.43 mL/min into a solution of azacrown ether (**1**−**6**) (3.0−6.0 mM) placed in the calorimeter. To obtain the net heat of complexation ($Q_{\mathrm{net}}$), the total apparent heat observed ($Q_{\mathrm{obs}}$) was corrected for the dilution of titrant ($Q_{\mathrm{D}}$), the nonchemical contributions ($Q_{\mathrm{HL}}$), including agitation, heat flow between the vessel and its surrounding, and resistance heating by the thermistor used, and the temperature difference between titrant and titrate ($Q_{\mathrm{TC}}$) in each run: $Q_{\mathrm{net}} = Q_{\mathrm{obs}} - Q_{\mathrm{D}} - Q_{\mathrm{HL}} - Q_{\mathrm{TC}}$. A titration curve was obtained by plotting the temperature change (measured by voltage) against the amount of the azacrown ether solution added, from which the complex stability constant ($K_s$) and the enthalpy change ($\Delta H°$) were directly calculated. Reliability of the whole system and the calculation procedures were doubly checked as previously[1] by comparison of the obtained thermodynamic data with the reported values[3,23] to give satisfactory results.

**Table 1. Complex Stability Constant (log $K_s$) and Thermodynamic Parameters (in kcal/mol) for Complexation of Alkali Metal Ions with Azacrown Ethers 1−6 in Methanol at 25 °C**

| crown ether | lanthanoid | log $K_s$ | $-\Delta G°$ | $-\Delta H°$ | $T\Delta S°$ | ref |
|---|---|---|---|---|---|---|
| **1** | Na$^+$ | 1.80 ± 0.03 | 2.46 | 6.52 ± 0.07 | −4.06 | *a* |
| | K$^+$ | 1.72 ± 0.03 | 2.35 | 8.15 ± 0.05 | −5.80 | *a* |
| **2** | Na$^+$ | 3.31 ± 0.06 | 4.27 | 4.63 ± 0.08 | −0.36 | *a* |
| | K$^+$ | 2.20 ± 0.07 | 3.00 | 11.69 ± 0.09 | −8.69 | *a* |
| | Cs$^+$ | 2.06 ± 0.02 | 2.81 | 5.86 ± 0.03 | −3.05 | *b* |
| **3** | Na$^+$ | 2.49 ± 0.03 | 3.40 | 6.62 ± 0.06 | −3.22 | *b* |
| | K$^+$ | 1.83 ± 0.03 | 2.50 | 15.12 ± 0.12 | −12.62 | *b* |
| | Cs$^+$ | 1.37 ± 0.03 | 1.87 | 15.74 ± 0.06 | −13.87 | *b* |
| **4** | Na$^+$ | 3.57 ± 0.03 | 4.87 | 5.89 ± 0.09 | −1.02 | *b* |
| | K$^+$ | 5.00 ± 0.07 | 6.82 | 11.27 ± 0.14 | −4.45 | *b* |
| | Cs$^+$ | 3.39 ± 0.06 | 4.62 | 11.84 ± 0.05 | −7.22 | *b* |
| **5** | Na$^+$ | 2.00 ± 0.08 | 2.73 | 3.66 ± 0.05 | −0.93 | *b* |
| | K$^+$ | 4.67 ± 0.06 | 6.34 | 9.01 ± 0.07 | −2.67 | *b* |
| | Cs$^+$ | 3.97 ± 0.08 | 5.42 | 8.63 ± 0.04 | −3.21 | *b* |
| **6** | Na$^+$ | 1.67 ± 0.06 | 2.28 | 4.62 ± 0.03 | −2.34 | *b* |
| | K$^+$ | 2.66 ± 0.03 | 3.63 | 10.73 ± 0.04 | −7.10 | *b* |
| | Cs$^+$ | 3.65 ± 0.06 | 4.98 | 9.71 ± 0.07 | −4.73 | *b* |

[a] Reference 1. [b] This work; values are the averages of more than three independent measurements.

## Results

Assuming the 1:1 stoichiometry for the complexation of alkali metal ions (M = Na$^+$, K$^+$, and Cs$^+$) with the azacrown ethers **1**−**6** (ACE in eq 1), the complex stability constant ($K_s$) and the enthalpy change ($\Delta H°$) were calculated by using the least-squares method to minimize the $U$ value (eq 2):[24,25]

$$\mathrm{ACE} + \mathrm{M} \overset{K_s}{\rightleftharpoons} \mathrm{ACE{\cdot}M} \tag{1}$$

$$U(K_s,\Delta H°) = \sum_{t=1}^{m} (Q_t - \Delta H° \times N_t)^2 \tag{2}$$

where $Q_t$ refers to the net heat of complexation measured at time $t$ in minutes, and $N_t$ denotes the amount in moles of the complex formed at time $t$ and is directly related to the complex stability constant $K_s$.

The stability constant $K_s$ and the enthalpy change $\Delta H°$ for the complexation of Na$^+$, K$^+$, and Cs$^+$ with **1**−**6** were calculated by computer simulation by continuously changing $K_s$, i.e., $N_t$, to minimize the $U$ value. For each cation−azacrown ether combination, the measurement was repeated more than three times, and the $U$ value obtained was minimized satisfactorily in each case to give the optimized set of $K_s$ and $\Delta H°$. No serious deviation was found in the fitting process, verifying the 1:1 stoichiometry of complexation as assumed above. The values obtained by the repeated measurements were averaged to give the complex stability constants and thermodynamic parameters with standard deviations (Table 1).

## Discussion

**Complex Stability and Cation Selectivity.** As can be seen from Table 1, the complex stability constant, relative cation selectivity, and thermodynamic parameters for the complexation reactions of alkali metal ions

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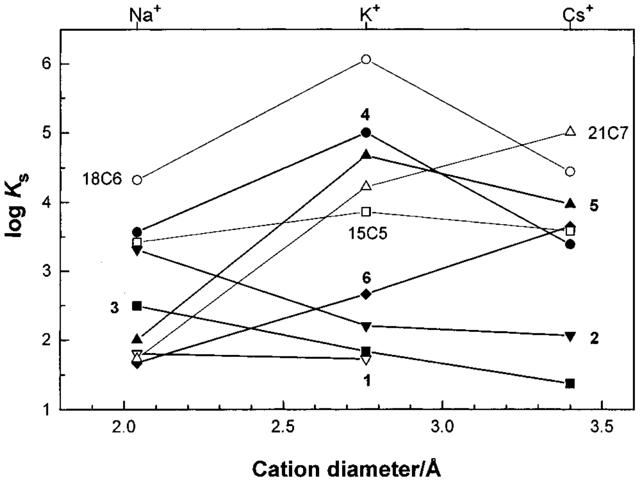

**Figure 1.** Complex stability constants ($K_s$) as a function of cation diameter for the complexation of azacrown ethers **1**−**6** and 15-crown-5 (15C5), 18-crown-6 (18C6), and 21-crown-7 (21C7) with alkali metal ions in methanol at 25 °C.

with azacrown ethers **1**−**6** are evidently influenced by several factors, particularly the bulkiness and/or flexibility of the substituent introduced at the *N*-pivot and the relative size between the ligand's cavity and the cation's diameter. The changing profile of complex stability constant ($K_s$) is plotted against the cation diameter in Figure 1. As a control, the data[28] for the parent 15-crown-5, 18-crown-6, and 21-crown-7 are also plotted in Figure 1.

It is noted that, possessing similar cavity sizes, three aza-15-crown-5 **1**−**3** display completely different complexation behavior, which may be attributed to the different substituent introduced at the *N*-pivot. Since the solvation energies for $Na^+$ to $Cs^+$ do not differ substantially even in water,[26] these differences observed are considered to arise from the other factors. Although all the aza-15-crown-5 derivatives show the inherent preference for $Na^+$, the complex stability constant and the relative cation selectivity for $Na^+$ over $K^+$ are dramatically affected by the *N*-substituent introduced. Interestingly, the *N*-octyl derivative **2** gives much higher log $K_s$ values and $Na^+/K^+$ selectivity than the phenyl and benzyl analogues **1** and **3** do. It is deduced therefore that the steric hindrance around the *N*-pivot plays a definitive role in determining the spacial arrangement and orientation of the crown's donor atoms. Probably, the octyl group induces most favorable conformation for the size-matched $Na^+$, while the benzyl or phenyl substitution at the *N*-pivot leads to less favorable conformations. However, the effects of the steric hindrance do not appear to be serious for the larger cations. Thus, the extent of decrease in log $K_s$ for $K^+$ is much smaller than that for $Na^+$ with **2**, which affords the highest $Na^+/K^+$ selectivity, up to 13. In the case of the phenyl derivative **1**, the reduced electron density of the nitrogen donor due to the electron-withdrawing effect of the phenyl substituent may be additionally responsible for its decreased complex stability.

In this context, it is interesting and somewhat puzzling that the parent aza-15-crown-5 without any steric hindrance around the nitrogen atom gives the smallest log $K_s$ values of 1.70 and 1.60 for $Na^+$ and $K^+$, respectively.[19,27] Possibly, the parent aza-15-crown-5, without any *N*-substituent that can lock the ring conformation, suffers substantial conformational changes upon cation binding, accompanying a considerable entropic loss that diminishes the complex stability.

More consistent results were obtained with the *N*-benzylazacrown ethers of varying ring sizes. As can be seen from Figure 1, the 15-, 18-, 21-, and 24-membered azacrown ethers (**3**, **4**, **5**, and **6**) show the highest log $K_s$ values for the size-matched cations, i.e., $Na^+$, $K^+$, and $Cs^+$, respectively. However, the highest complex stability constant for $Na^+$ was obtained not with aza-15-crown-5 **3** but with aza-18-crown-6 **4**. One possible rationalization would be that the steric hindrance caused by the *N*-benzyl group makes the operation of strict size-fitting difficult. Alternatively, the tendency of alkali metal ions to form hexacoordinated complexes with crown ethers[19] would also give the higher $K_s$ for crown-6 rather than crown-5.[28] However, it is interesting that the increased steric hindrance in benzyl azacrown ethers enhances the relative cation selectivities for $Na^+$, $K^+$, and $Cs^+$ as compared with the unsubstituted 15-crown-5 to 24-crown-8,[28] see Figure 1. The relative selectivities of $Na^+/K^+$ for **3** and $K^+/Cs^+$ for **4** are 4.6 and 40.7, respectively, while *N*-benzylaza-24-crown-8 (**6**) gives a high $Cs^+/K^+$ selectivity of 9.8.

**Thermodynamic Parameters.** To discuss the $K_s$ and relative cation selectivity from the thermodynamic point of view, thermodynamic quantities obtained are plotted in Figure 2. It is intriguing that all the enthalpy changes ($\Delta H°$) are negative and so are the entropy changes ($\Delta S°$). These results indicate that the complexation of azacrown ethers **1**−**6** with the alkali metal ions examined is driven predominantly by the favorable enthalpic gains, mostly originating from the strong ion−dipole interactions. However, the individual complex stability and cation selectivity are controlled primarily by the entropic term, arising from the ligand's conformational changes and the desolvation from both cation and ligand. Thus, the preferred binding ability of **2** for $Na^+$ is not the result of the largest enthalpic gain ($-\Delta H°$) but the smallest entropic loss ($\Delta S°$), and the other cation−ligand combinations exhibit quite similar thermodynamic behavior, as can be observed from the data in Figure 2. Consequently, large enthalpic gain ($-\Delta H°$) does not immediately mean high complex stability and is often canceled by larger entropic loss ($T\Delta S°$), as exemplified by the complexation behavior of *N*-benzylaza-15-crown-5 (**3**) with $K^+$ and $Cs^+$. Instead, the cation−crown ether combinations with smaller entropic losses lead to higher complex stabilities.

It is interesting to compare the thermodynamic parameters for the complexation of a series of benzylazacrown ethers **3**−**6** with $K^+$ and $Cs^+$. As can be seen from Table 1 and Figure 2, the enthalpy changes for $K^+$ and $Cs^+$ are nearly equal to each other within <1 kcal/mol for these azacrown ethers (**3**−**6**), indicating comparable ion−dipole interaction for these cations, irrespective of the ligand's ring size. However, the entropy changes differ substantially between these two cations except for the size-mismatched ligand **3**. Thus, the cations size-fitted to the ligand's cavity, i.e., $K^+$ for **4**, and **5**, and $Cs^+$

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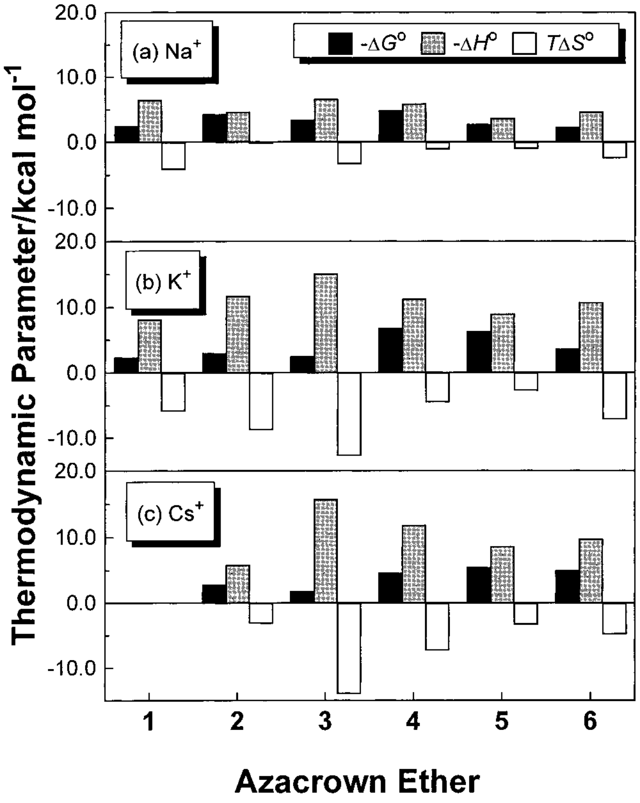

**Figure 2.** Thermodynamic parameters for the complexation of azacrown ethers **1**–**6** with alkali metal ions: (a) Na$^+$, (b) K$^+$, and (c) Cs$^+$ in methanol at 25 °C.

for **6**, afford much reduced entropic losses. The minimized entropic loss may be rationalized by the fact that the size-fitted cation suffers more extensive desolvation upon complexation than the mismatched one, compensating for a substantial part of the inherent entropic decrease from the complex formation.

Another interesting thermodynamic feature is the changing profile of the $\Delta H°$ and $\Delta S°$ values observed for ligands **3**–**6** and the compensation between these terms. For this series of ligands, the enthalpic gain ($-\Delta H°$) and the entropic loss ($T\Delta S°$) obtained for ligands **3**–**6** increase simultaneously with increasing cation diameter in a compensatory manner. This kind of enthalpy–entropy compensation effect has been observed widely in supramolecular interactions and discussed earlier from a more global point of view.[24,25,29] In general, the larger enthalpic gain leads to stronger host–guest interaction producing a more rigid complex with reduced freedom, which entropically cancels the enthalpic gain at least in part. In the present case, it is somewhat unexpected however that the size-matched cation–ligand combinations do not necessarily give the largest enthalpic gains; see data for K$^+$–**4** and Cs$^+$–**6** combinations. Furthermore, it is a general tendency that the complexations with larger cations (K$^+$ and Cs$^+$) afford greater enthalpic gains (and entropic losses), irrespective of the ligand's ring size. Typically, aza-15-crown-5 **3** affords the largest enthalpic gain not with the size-matched Na$^+$ but with much larger-sized Cs$^+$. A plausible explanation of this general tendency is that the complex formation of azacrown ethers is not driven by equal participation of all donor atoms but by preferential interaction with the nitrogen donor which is assisted by the oxygen donors. Hence, the interaction of a soft nitrogen donor with soft cations (K$^+$ and Cs$^+$) produces more heat ($-\Delta H°$) and accompanying entropic loss ($T\Delta S°$) than a hard cation (Na$^+$).

This simple idea may also explain the changing profile of thermodynamic parameters obtained for the complexation of **3**–**6** with soft cations. Regardless of the increased number of formal donor atoms, the enthalpic gain and entropic loss gradually decrease with the ligand's increasing size up to 21 and then increase to some extent (Figure 2). This behavior suggests that the oxygen atoms in smaller ligand are situated in the correct position and/or orientation to be suitable for cation binding and only a limited number of oxygen atoms around the *N*-pivot can coordinate to the cation accommodated in larger ligands up to 21-crown-7, while the donor atoms in the largest 24-crown-8 can wrap around the cation, showing recovery in $\Delta H°$ and $T\Delta S°$.

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**Supporting Information Available:** Calorimetric titration data and detailed calculation procedures for the 1:1 complexation of sodium chloride with *N*-benzylaza-18-crown-6 (**4**) (4 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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