

# The Complexation of Alkali Metal Ions by Crown Ethers, Aza Crown Ethers, and Cryptands in Propylene Carbonate\*

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**Abstract.** The reactions between alkali metal ions and crown ethers, aza crown ethers, and cryptands in propylene carbonate were studied by potentiometric and calorimetric titrations. The most stable complexes formed by macrocyclic and macrobicyclic ligands are when the ligand and cation dimensions are comparable. On comparing the complex stabilities of crown ethers and aza crown ethers of the same size, crown ethers were, on the whole, found to form the most stable complexes, with the exception of the lithium cation. Enthalpic factors are responsible. Substitution of the amino group protons of the aza crown ethers by benzyl groups leads to a high increase in values of the reaction enthalpy. This effect is partly compensated by entropic contributions. The bulky benzyl groups reduce the ligand solvent interactions and induce a ligand conformation with the lone pair of electrons from the nitrogen donor atoms which are more or less directed inside the cavity. The thermodynamic data for the transfer from methanol to propylene carbonate indicate that the ligands containing nitrogen show specific interactions with methanol.

**Key words.** Crown ethers, cryptands, solvent influence.

## 1. Introduction

The solvents most frequently used for the study of complexation reactions between alkali ions and synthetic macrocyclic and macrobicyclic ligands are methanol and water [1]. The influence of the different solvents upon these reactions is not only restricted to differences in the solvation of the cations. The interactions between crown ethers and solvent molecules also play an important role [2, 3]. The macrobicyclic ligands are also influenced by the surrounding solvent. Thus, the conformational kinetics of the cryptand (222) are dependent upon the nature of the solvent [4]. NMR spectra of the uncomplexed cryptand (221) show specific ligand–solvent interactions [5]. For both ligands they have been interpreted as hydrogen bonds between the solvent molecules and the ligands.

Thus, the solvation of the cations and ligands contributes to the overall experimental effect observed in the form of the stability constants and the reaction enthalpies and entropies. During the formation of the complex the cation will in any case be partly or completely desolvated. The desolvation is an endothermic reaction and the complexation is an exothermic one. Ligand interactions with surrounding solvent molecules will also reduce the exothermicity. On the other hand the liberation of solvent molecules bound to the cation and to the ligand result in

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positive entropic changes which favour the complex formation. The stability of the complex formed in both processes of solvation is influenced in an opposite way by the enthalpic and entropic contributions. It would seem that they may eliminate each other on some occasions which suggests that the stability constant is not dependent on the solvents used.

In the present study, the solvent selected was propylene carbonate. On comparison with methanol, one establishes some important differences in the solvent properties. Propylene carbonate is an aprotic solvent with a high dielectric constant ( $\epsilon = 66.1$ ) and a low donor number ( $DN = 15.1$ ) [6]. In contrast, methanol is a protic solvent with a lower dielectric constant ( $\epsilon = 32.7$ ) but a higher donor number ( $DN = 30.1$ ) [6]. Thus, on studying the complexation reactions in propylene carbonate in detail one expects to gain further insight into the role of the solvent. Up to now the experimental data on this solvent has been minimal.

## 2. Experimental

The crown ethers 15-crown-5 (15C5), 18-crown-6 (18C6), the aza crown ethers (21), (22), and the cryptands (211), (221), and (222) were obtained from Merck and were used without further purification. The aza crown ethers (21TT) and (22TT) were synthesized and purified as already described in the literature [7, 8].

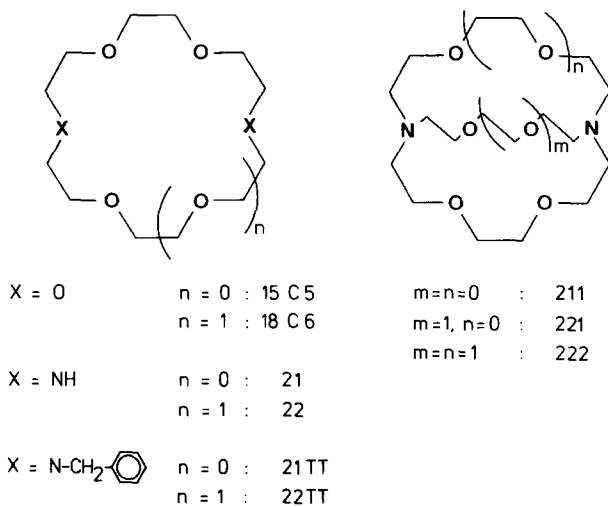


Fig. 1. Macrocyclic and macrobicyclic ligands used in this work.

The anhydrous metal salts used were  $\text{LiClO}_4$  (Ventron),  $\text{NaClO}_4$  (Ventron),  $\text{NaBPh}_4$  (Fluka). Other alkali tetraphenylborates were prepared according to well known procedures [9]. As the solvent, propylene carbonate (Merck, p.A.) was used. The water content, estimated by Karl-Fischer titration, was less than 0.1%.

In solution the following reaction between an alkali ion  $M^+$  and a ligand molecule  $L$  takes place:



The stability constant is given by:

$$K = \frac{[ML^+]}{[M^+][L]}$$

Stability constants smaller than  $10^5 \text{ M}^{-1}$  and all reaction enthalpies were determined by titration calorimetry using a Tronac Model 450 calorimeter. A solution of the ligand (0.02–0.04M) is titrated continuously in a salt solution ( $1-2.5 \times 10^{-3}\text{M}$ ). The procedure used to calculate the stability constant of the complex formed from the thermogram simultaneously with the corresponding reaction enthalpy has already been described elsewhere [10, 11, 12]. The stability constant is valid at an ionic strength of zero since correction to the activity coefficient is made using the Debye–Hückel expression. The accuracy of the calorimeter used has already been tested by measuring the heat of protonation of trishydroxymethylaminomethane in water [13].

Additionally direct potentiometric titrations were performed using ion selective electrodes for  $\text{Na}^+$  (Metrohm EA 109-Na) and  $\text{K}^+$  (Ingold pk 201-S7). Other stability constants were measured using disproportionate potentiometric titrations with  $\text{Ag}^+$  [14]. The potentiometric titrations of solutions containing  $\text{K}^+$  with the crown ether 15C5 and the cryptand (211) gave clear evidence of the formation of complexes with other than 1:1 stoichiometry. This subject has already been dealt with in detail [15].

During all potentiometric titrations the ionic strength was  $5 \times 10^{-2} \text{ M}$  and  $\text{N}(\text{C}_2\text{H}_5)_4\text{ClO}_4$  (Fluka) was used as the supporting electrolyte. The influence of the ionic strength  $I$  on the value of the concentration stability constant is known to be rather small even at  $I = 0.05 \text{ M}$  [16].

The calorimetric and potentiometric titrations were performed at least three times. The uncertainty in  $\log K$  is  $\pm 0.02$  if potentiometric titrations were used and  $\pm 0.05$  in the case of calorimetric titrations. The reproducibility of the values of the reaction enthalpies was  $\pm 1 \text{ kJ mol}^{-1}$ .

### 3. Results and Discussion

The values of  $\log K$ ,  $\Delta H$ , and  $T \Delta S$  for the complexation of alkali ions by different macrocyclic and macrobicyclic ligands are summarized in Table I. For comparison some stability constants of alkali complexes with these ligands in propylene carbonate are summarized in Reference [1]. More recently further stability constants for the complexation reactions of 18C6, the diaza crown ether (22) [2], and the cryptands (211) and (221) [17] have been reported. However, reaction enthalpies are only known for the reaction of 18C6 with  $\text{Li}^+$  [18] and for the reactions of (222) with alkali ions [19]. These values are similar to those given in Table I. Neither stability constants nor reaction enthalpies for the reactions of the ligands (21), (21TT), and (22TT) are available from the literature.

The cavity diameter of the ligands used and the ionic radii of alkali ions are listed in Table II. The ligands form very stable complexes if the cavity and cation dimensions are equal. In this case optimal interactions between all the ligand donor atoms and the complexed cations are possible as can be seen in the case of the complex formation between the cryptand (211) and  $\text{Li}^+$ , the cryptand (221) and

Table I. Stability constants ( $\log K$ ;  $K$  in  $M^{-1}$ ) and thermodynamic parameters ( $\Delta H$ ,  $T \Delta S$  in  $\text{kJ mol}^{-1}$ ) for the reaction of crown ethers and cryptands with alkali ions in propylene carbonate at  $25^\circ\text{C}$

Ligand	Parameter	$\text{Li}^+$	$\text{Na}^+$	$\text{K}^+$	$\text{Rb}^+$	$\text{Cs}^+$
15C5	$\log K$	4.03	4.87	3.78	3.74	3.39
	$-\Delta H$	20.8	31.9	30.5 <sup>a</sup>	26.0	17.0
	$T \Delta S$	2.1	-4.2	-9.0 <sup>a</sup>	-4.7	2.3
18C6	$\log K$	2.70	4.55 <sup>b</sup>	6.08 <sup>a</sup>	5.33 <sup>c</sup>	4.48
	$-\Delta H$	17.0	28.7	45.4 <sup>a</sup>	44.2	42.9
	$T \Delta S$	-1.7	-2.8	-10.9 <sup>a</sup>	-13.9	-17.4
21	$\log K$	4.12	4.83	2.25 <sup>a</sup>	- <sup>d</sup>	- <sup>d</sup>
	$-\Delta H$	16.3	18.1	7.7 <sup>a</sup>		
	$T \Delta S$	7.1	9.3	5.1 <sup>a</sup>		
21TT	$\log K$	4.19	4.66 <sup>c</sup>	3.37 <sup>c</sup>	2.55	- <sup>d</sup>
	$-\Delta H$	31.1	35.6	30.3	23.4	
	$T \Delta S$	-7.3	-9.1	-11.2	-8.9	
22	$\log K$	3.59 <sup>c</sup>	4.31 <sup>c</sup>	4.43 <sup>a</sup>	2.93 <sup>c</sup>	- <sup>d</sup>
	$-\Delta H$	5.8	13.1	21.9 <sup>a</sup>	7.8	
	$T \Delta S$	14.6	11.4	3.3 <sup>a</sup>	8.8	
22TT	$\log K$	4.32 <sup>c</sup>	4.94 <sup>c</sup>	4.56 <sup>e</sup>	3.69	3.63
	$-\Delta H$	36.7	39.8	45.3	39.0	22.2
	$T \Delta S$	-12.2	-11.7	-19.4	-18.0	-1.6
211	$\log K$	13.7 <sup>c</sup>	8.90 <sup>c</sup>	3.50 <sup>a</sup>	2.69	2.58
	$-\Delta H$	70.6	52.5	30.0 <sup>a</sup>	16.3	4.7
	$T \Delta S$	7.2	-1.9	-10.1 <sup>a</sup>	-1.0	10.0
221	$\log K$	11.5 <sup>c</sup>	11.86 <sup>c</sup>	9.15 <sup>a</sup>	7.26 <sup>c</sup>	4.43
	$-\Delta H$	50.8	68.1	66.0 <sup>a</sup>	54.7	48.2
	$T \Delta S$	14.5	-0.7	-14.0 <sup>a</sup>	-13.4	-23.0
222	$\log K$	6.77 <sup>c</sup>	10.29 <sup>c</sup>	11.00 <sup>a</sup>	9.10 <sup>c</sup>	4.19
	$-\Delta H$	35.9	67.5	72.8 <sup>a</sup>	70.6	42.9
	$T \Delta S$	2.6	-9.0	-10.3 <sup>a</sup>	-18.9	-19.1

<sup>a</sup> from Ref. [15].

<sup>b</sup> sodium selective electrode.

<sup>c</sup> from a disproportionate potentiometric titration with  $\text{Ag}^+$ .

<sup>d</sup> the heat produced during the titration was too small to calculate, values of  $\log K$  or  $\Delta H$  from the thermogram.

<sup>e</sup> potassium selective electrodes.

$\text{Na}^+$ , and the cryptand (222) and  $\text{K}^+$ . Therefore these complexes are the most stable ones compared with the other cations. Also, the formation of the complexes mentioned above is accompanied by the highest values of the reaction enthalpies in comparison with the other alkali metal ions.

If the cation is too small in comparison with the cavity dimensions, the ligand has to adapt to an unfavourable conformation in order to achieve interactions between the cation and the donor atoms. This can easily be seen from the reaction enthalpies

Table II. Cavity radii of crown ethers and cryptands and ionic radii of alkali ions

Ligand	Radius $r[\text{\AA}]$	Cation	Radius $r[\text{\AA}]$
15C5, (21), (21TT)	0.9 <sup>a</sup>	Li <sup>+</sup>	0.73 <sup>c</sup>
18C6, (22), (22TT)	1.4 <sup>a</sup>	Na <sup>+</sup>	1.02 <sup>c</sup>
(211)	0.8 <sup>b</sup>	K <sup>+</sup>	1.38 <sup>c</sup>
(221)	1.1 <sup>b</sup>	Rb <sup>+</sup>	1.49 <sup>c</sup>
(222)	1.4 <sup>b</sup>	Cs <sup>+</sup>	1.70 <sup>c</sup>

<sup>a</sup> from Ref. [28].

<sup>b</sup> from Ref. [29].

<sup>c</sup> from Ref. [30].

for the complexation of Li<sup>+</sup> by cryptands. The measured values of the reaction enthalpies decrease when the size of the cavity and the number of cryptand donor atoms increases.

Cations which are too big to fit into the cavity are not able to interact optimally with all donor atoms. In this case the complexed cation is located above the crown ether or the cavity of the cryptands may even be deformed by these cations. In both cases a reduction in the values of the reaction enthalpies is expected. This is responsible for the low values of the reaction enthalpy for the reaction of the crown ether 15C5 and the cryptand (211) with Cs<sup>+</sup>. Interestingly, it is of importance for the complexation of Cs<sup>+</sup> if the ligand is macrocyclic or macrobicyclic as can easily be seen from the values given in Table I for the diaza crown ethers and cryptands.

An identical interpretation is possible for the results found for crown ethers. The stability of the sodium complex of 15C5 is slightly higher when compared with 18C6. However, the crown ether 18C6 has one more donor atom than the ligand 15C5 which in addition interacts with the complexed ion. This is obviously compensated by a reduction in the interactions between the donor atoms and the cation which are caused by the difference between cation and cavity dimensions.

In the case of the reaction of K<sup>+</sup> with the ligands 15C5 and 18C6 different results are obtained. The complex with the crown ether 18C6 is several orders of magnitude more stable than the 15C5 complex. This increase is only achieved with favourable enthalpic contributions. The potassium ion and the cavity of 18C6 have the same radii.

The interpretation of the results for other cations follows the one given above. Thus, no deviation from the cation diameter-hole size relationship is found in propylene carbonate for the reactions of crown ethers and cryptands. The reliability of this relationship has been doubted for the complexation of Na<sup>+</sup> and K<sup>+</sup> by crown ethers in methanol [20].

The complexation behaviour of the diaza crown ethers (21) and (22) is quite different. However, the most stable complexes are formed again if cation and cavity radii are of comparable size. The values of the reaction enthalpies for the complexation reactions of the ligands (21) and (22) are smaller compared with the analogous crown ethers. In contrast, the complex formation of aza crown ethers is favoured by entropic factors.

For every ligand the contributions to the total estimated reaction entropy [21] are:

- (a) part of complete desolvation of the cation;
- (b) changes in the ligand solvation;
- (c) changes in the ligand internal entropy due to orientation, rigidification and conformational changes;
- (d) variation in the number of particles during the reaction;
- (e) changes in translational entropy.

In the case of monocyclic ligands the factors (a) and (e) are independent of the nature of the ligand. Therefore, the contributions (b), (c), and (d) depend on the ligand structure. It is not possible to divide the reaction entropies measured into corresponding parts. Some further insight into the importance of the different factors is possible from the results for the complexation reactions of the aza crown ethers (21TT) and (22TT). The protons of the amino groups were substituted by bulky groups which contain no additional donor atoms. However, the exothermicity increases when compared with the ligands (21) and (22). On the other hand, negative reaction entropies are not favourable to the complexation reaction with (21TT) and (22TT). These reaction entropies of the ligands (21TT) and (22TT) are comparable with those observed for crown ethers. Since no interactions between the bulky groups of the ligands (21TT) and (22TT) and the cations are possible they obviously influence the interactions between the aza crown ethers and solvent molecules and the conformation of the uncomplexed ligand. Using CPK models of the diaza crown ethers one finds that the bulky groups force the uncomplexed ligand to adapt to a conformation where the lone pair of electrons of both nitrogen atoms are more or less orientated into the cavity. The unsubstituted aza crown ethers have to adopt this conformation during the reaction. It is energetically unfavourable since the dipoles of all donor atoms are directed into the cavity. If the interactions between the nitrogen donor atoms and solvent molecules are reduced the cations displace these solvent molecules more easily.

This interpretation explains the difference in the reaction enthalpies observed between the ligands (21) and (21TT) and also between (22) and (22TT).

The reduction of ligand-solvent interactions results in a negative contribution to the reaction entropy since the number of solvent molecules liberated during complex formation decreases. From the reaction entropies for the diaza crown ethers given in Table I one finds at 25°C:  $T \Delta S(21) - T \Delta S(21TT) = 16 \pm 2 \text{ kJ mol}^{-1}$  and  $T \Delta S(22) - T \Delta S(22TT) = 25 \pm 2 \text{ kJ mol}^{-1}$ .

The number of solvent molecules released obviously depends on the size of the ligands. The entropy of freezing at 25°C of propylene carbonate is  $T \Delta S_{\text{freeze}} = -9.0 \text{ kJ mol}^{-1}$  [22]. Using this value for an approximate estimation of the number of solvent molecules liberated from the ligand during complex formation with cations, one finds in the first case that approximately two and in the second three solvent molecules bound to the diaza crown ethers are set free. As a result, positive reaction entropies are found for the diaza crown ethers (21) and (22). However, since other factors influencing the reaction entropies – such as changes in the ligand internal entropy – have been neglected this interpretation can only demonstrate general trends.

As in other solvents the most stable complexes are formed by the macrobicyclic cryptands if real inclusion complexes are formed. Cations too big to be encapsulated into the cavity of the ligand can only form exclusive complexes [23]. All cryptand complexes with  $\text{Cs}^+$  belong to this complex type. The stability constants for real inclusion complexes formed in propylene carbonate are higher or equal when compared with the results obtained in methanol [24].

By combining stability constants measured in methanol and propylene carbonate solutions with thermodynamic data on the solvation of  $\text{M}^+$  and the ligand, it is possible to gain information on the solvent dependence of the complex formation. The free energy of transfer for the complex from one solvent to another can be calculated using the following equation

$$\Delta G_{\text{tr}}(\text{ML}^+) = \Delta G_{\text{tr}}(\text{L}) + \Delta G_{\text{tr}}(\text{M}^+) - 2.303 RT \log[K(\text{MeOH})/K(\text{PC})]$$

Similar equations were used to deduce the enthalpy and entropy of transfer. Further discussion will be restricted to the  $\text{K}^+$  ion because it fits excellently inside the ligand cavity of the cryptand (222), the crown ether 18C6 and the corresponding diaza crown ethers. Thus, no effects due to reduced interactions between other complexed cations and all the ligands examined need to be discussed further. Using the above given equation and the tabulated values for the transfer of  $\text{K}^+$  from methanol to propylene carbonate [25]

$$\Delta G_{\text{tr}} = -4.3(\text{kJ mol}^{-1})$$

$$\Delta H_{\text{tr}} = -3.5(\text{kJ mol}^{-1})$$

$$\Delta S_{\text{tr}} = 5(\text{J mol}^{-1} \text{K}^{-1})$$

one gets the values summarized in Table III. Since values for the transfer of the pure ligands are only known for the ligands (22) [26] and (222) [27] only the quantities  $\Delta G_{\text{tr}}(\text{ML}^+) - \Delta G_{\text{tr}}(\text{L})$ ,  $\Delta H_{\text{tr}}(\text{ML}^+) - \Delta H_{\text{tr}}(\text{L})$  and  $\Delta S_{\text{tr}}(\text{ML}^+) - \Delta S_{\text{tr}}(\text{L})$  can be given.

The thermodynamic data for the transfer from methanol to propylene carbonate vary from ligand to ligand. One would expect that the data for monocyclic ligands are similar since the complexed cation is still in contact with the solvent. However, in the case of the free energies of transfer it seems to be more important whether the ligand contains nitrogen atoms or not. The free energies of transfer of the crown ethers 15C5 and 18C6 are almost identical. The corresponding values for the diaza crown ethers and cryptands are much higher when compared with the former. The stronger solvation of diaza crown ethers and cryptands and their complexes in methanol is probably because of hydrogen bonding.

Table III. Thermodynamic values of transfer of  $\text{K}^+$ -complexes from methanol to propylene carbonate at 25°C ( $\Delta G$ ,  $\Delta H$  in  $\text{kJ mol}^{-1}$  and  $\Delta S$  in  $\text{J K}^{-1} \text{mol}^{-1}$ )

Parameter	15C5	18C8	21	22	22TT	211	221	222
$\Delta G_{\text{tr}}(\text{ML}^+) - \Delta G_{\text{tr}}(\text{L})$	-3.9	-3.1	-	-19.1	-11.2	-10.8	-8.6	-7.2
$\Delta H_{\text{tr}}(\text{ML}^+) - \Delta H_{\text{tr}}(\text{L})$	-3.0	6.0	-	-20.7	-10.3	3.3	-8.4	-1.3
$\Delta S_{\text{tr}}(\text{ML}^+) - \Delta S_{\text{tr}}(\text{L})$	3.0	30.5	-	-5.4	3.0	47.3	0.7	19.8

A detailed discussion of the enthalpies and entropies of transfer is not possible at the moment since with the exception of the cryptand (222) [26] the data for the transfer of ligands are not known. A net loss of hydrogen bonds on going from one solvent to another should result in large positive values of  $\Delta H_{tr}$  and  $\Delta S_{tr}$ . However, the values in Table III indicate a more complex situation.

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