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The Macrocyclic and Cryptate Effects.
5. Complexation of Alkali Ions by Monocyclic and Bicyclic Ligands in Methanol

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Abstract

The complexation of alkali ions by the ligand 18-crown-6 and by different azacrown ethers and cryptands was studied in methanol by calorimetric and potentiometric titrations. The macrocyclic effect found for the reactions of 18-crown-6 is caused only by favourable entropic changes. Due to the different conformational forms of the uncomplexed azacrown ethers, their complexes with alkali ions are not as stable as the complexes of unsubstituted crown ethers. Cations too big to be encapsulated by the bicyclic cryptands form exclusive complexes. However, 2:1 complexes could not be observed in these cases. During the complex formation the cryptands have to change their conformation. Therefore, the observed reaction enthalpies are smaller than expected. On the other hand, the stability constants measured for the reactions of bicyclic ligands with alkali ions are several orders of magnitude higher in most cases in comparison with monocyclic ligands. It is concluded that the macrocyclic and cryptate effects are caused only by favourable entropic changes.

Introduction

Comparing the measured stability constants of nitrogen-containing noncyclic ligands with their macrocyclic analogues, a 'macrocyclic effect' was observed [1]. The same effect was found using ligands containing only oxygen donor atoms [2]. The origin of the so-called 'macrocyclic effect' for complexes with nitrogen macrocycles has, up to now, not been well established [3]. The discussion of the results obtained with other cyclic ligands is rather complicated, too. There is no consistent interpretation possible of experimental findings obtained so far [4].

The bicyclic cryptands are able to complex cations more strongly than the monocyclic ligands. The increase in complex stability was interpreted to be caused by a 'cryptate effect' [5]. On the other hand, neither a 'macrocyclic' nor a 'cryptate effect' was verified experimentally for the complexation of Ag^+, Hg^{2+} and Cd^{2+} in aqueous solutions [6].

In recent publications detailed experimental results explaining the origin of both effects in the case of Pb^{2+} [7], Ag^+ [8], Ba^{2+} [9], Co^{2+} and Ni^{2+} [10] were reported. For this series it was possible to obtain individual bond strengths of the cations attached to different donor atoms in methanol solution. With these values it became possible to discuss the enthalpic and entropic contributions to both effects. For other cations, especially the alkali ions, it was not possible to calculate individual bond strengths of the cations to oxygen donor atoms from experimental results [11]. This situation made it very difficult to give any meaningful explanation. Meanwhile, the study of the complexation reactions of polyethylenglycols with several cations in methanol solutions seems to elucidate the situation [12]. Thus, studies of the complexation of alkali cation by mono- and bicyclic ligands appeared to be most interesting. Considering all these experimental data, a discussion of the origin of the 'macrocyclic' and the 'cryptate effect' for the complexation of alkali ions should become possible now.

Experimental

The monocyclic and bicyclic ligands examined in this work are shown in Fig. 1. All ligands (Merck) were used without further purification. Before preparing the solutions, $NaNO_3$ (Merck), KJ (Merck), RbJ (Merck), $RbNO_3$ (Merck), CsF (Ventron) and $AgNO_3$ (Merck) were dried under vacuum. Anhydrous methanol (H_2O content less than 0.01%; Merck) was used as solvent. The different experimental methods to measure the stability constant and the reaction enthalpy for the reaction (1) have

$$M^+ + L \rightleftharpoons ML^+ \qquad K = \frac{[ML^+]}{[M^+][L]} \qquad (1)$$

been described elsewhere [7, 8]. Additionally, ion selective electrodes for Na^+ (Metrohm EA 109-Na)

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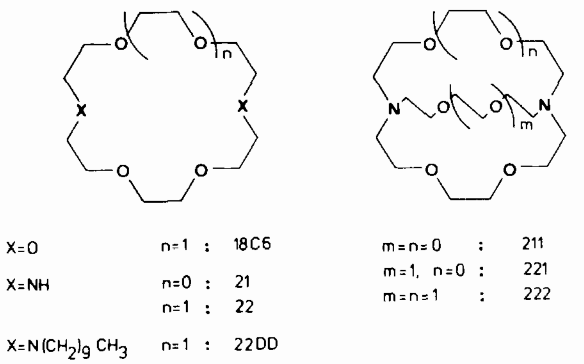

Fig. 1. Ligands used in this study.

and K$^+$ (Ingold pK 201-S7) were used. During calorimetric titrations of the ligands (21) and (22) to solutions containing an alkali salt, only very small temperature increases could be observed. To clarify the situation a solution of the bicyclic ligand (222) (0.08 N) was titrated into a solution containing the monocyclic ligand (21) or (22) (0.03 M) and an alkali salt (5 X 10^{-3} M). With one exception the observed reaction enthalpies were nearly identical to the ones obtained without the monocyclic ligand. Obviously, no reaction between the azacrown ethers and alkali ions was observable because the values of the reaction enthalpies for these reactions are nearly zero. Therefore, potentiometric competition reactions of alkali ions with Ag$^+$ in the presence of a ligand were performed. From these experiments it can be clearly concluded that no reactions between (21) and (22) and most alkali ions took place. The formation of complexes between the ligand (22DD) and alkali ions could be measured directly by means of calorimetric titrations.

Two different experimental techniques were used to detect the formation of 2:1 complexes between cryptands and cations: (a) A solution of an appropriate cation (0.08 N) was titrated into a ligand solution (5 X 10^{-3} N). (b) A solution of the cryptand (222) (0.04–0.08 N) was added to solutions containing the cryptand (211) (0.02–0.04 N) and an alkali ion (5 X 10^{-4}–5 X 10^{-3} N).

Results and Discussion

The values of log *K*, Δ*H*, and *T*Δ*S* for the reaction of alkali ions with monocyclic and bicyclic ligands are summarized in Table I. In the literature stability constants are available only for the azacrown ether (22) in methanol [2, 13]. More data are available for the reaction of cryptands with alkali ions. Thus, in the case of the bicyclic ligand (211) some stability constants have been published [14, 15]. Stabilities of the formed complexes and reaction enthalpies are reported for the ligand (221) [16, 17]. Different authors reported values of the stability constants of the (222) complexes [15, 18] and of the reaction enthalpies [19]. With some exceptions the measured values agree with the published ones. The azacrown ether (22) forms complexes which are several orders of magnitude less stable than the complexes of 18-crown-6. Substi-

TABLE I. Stability Constants (log *K*; *K* in M^{-1}) and Thermodynamic Parameters (Δ*H*, *T*Δ*S* in kJ mol^{-1}) for the Complexation of Alkali Ions by Crown Ethers and Cryptands in Methanol at 25 °C

Ligand	Value	Li$^+$	Na$^+$	K$^+$	Rb$^+$	Cs$^+$
18C6^a	log *K*	–	4.32	6.29	5.82	4.44
	–Δ*H*		34.0	54.9	49.6	49.9
	*T*Δ*S*		–9.5	–19.2	–16.5	–24.7
21	log *K*	–	–	–	–	–
22	log *K*	–	–	1.83	<1	–
	–Δ*H*			4.7	<2	
	*T*Δ*S*			5.7		
22DD	log *K*	–	3.02	4.00^b	3.51	3.08
	–Δ*H*		16.8	31.5	34.4	21.7
	*T*Δ*S*		0.4	–8.8	–14.5	–4.2
211	log *K*	7.90	6.64^b	2.36	2.50	2.50
	–Δ*H*	33.9	33.1	23.2	8.0	6.5
	*T*Δ*S*	11.0	4.6	–9.8	6.2	7.7
221	log *K*	4.69	9.71	8.40^b	7.35	4.32
	–Δ*H*	10.3	49.8	61.1	55.7	47.4
	*T*Δ*S*	16.3	5.4	–13.4	–13.9	–22.9
222	log *K*	2.46	7.97(7.95^b)	10.49(9.82^b)	9.10	3.95
	–Δ*H*	3.7	39.8	75.0	72.7	49.7
	*T*Δ*S*	10.3	5.5	–15.4	–21.0	–27.3

^{a}From ref. 22 and ref. 30. ^{b}Ion selective electrode.

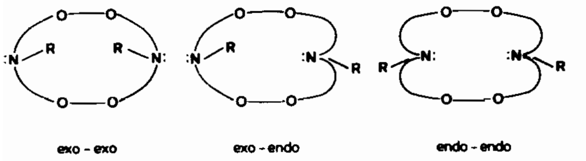

Fig. 2. Different conformational forms of uncomplexed azacrowns.

tution of the protons of the amino groups of (22) by long alkyl chains (22DD) leads to an increase of the measured reaction enthalpies. Thus, complexes with Na^+, K^+ Rb^+, and Cs^+ can be observed. Azacrown ethers and cryptands exist in different conformational forms [20] see Fig. 2. The long chains obviously shift the equilibrium to the *endo- endo* conformation. The ligands (21) and (22) have to adapt this conformation for sterical reasons during the complexation reactions. Therefore, the measured reaction enthalpies are reduced by the inversion energy of both nitrogen atoms.

The same effect should be observable for the reactions of the bicyclic ligands. The most stable complexes with alkali ions are found if the complexed cations fit optimally into the cavity of the cryptands, see Table II. From the reaction of the ligand (222) with Cs^+ it is known that no real inclusion compound is formed [21]. Parts of the Cs^+ ion still interact with solvent molecules. The same situation is observed for the reaction of the cryptand (211) with K^+, Rb^+, and Cs^+. The stability constants and the values for the reaction enthalpies for the reaction of the ligands (221) and (222) with Cs^+ are nearly identical. Therefore, both complexes formed are exclusive complexes.

TABLE II. Cation Ionic Radii for Alkali Ions and Cavity Radii of Crown Ethers and Cryptands

Cations	r (A)^a	Ligands	r (A)^b
Li^+	0.73	(21)	0.9
Na^+	1.02	18C6, (22)	1.4
K^+	1.38	(211)	0.8
Rb^+	1.49	(221)	1.1
Cs^+	1.70	(222)	1.4

^{a}From ref. 31. ^{b}From ref. 13.

Under these circumstances the formation of 2:1 complexes (ratio of ligand to cation) should be possible. Crown ether complexes of this composition have already been measured in solution [2, 22]. No direct evidence for the existence of cryptate complexes with 2:1 stoichiometry from potentiometric titrations has been found earlier [23]. However, such complexes were proposed as intermediates from kinetic measurements of ligand-exchange reactions of cryptands [24].

To detect 2:1 cryptate complexes by means of calorimetric tirations the concentration of the ligand has to be much higher than the concentration of the cation during the titration. This condition was fulfilled if a solution of CsF was titrated into a solution of the cryptand (222). From the thermogram the stability of the Cs^+ complex and a value for the reaction enthalpy were calculated assuming only the formation of a 1:1 complex. The following values were obtained: $\log K = 3.91$ (K in M^{-1}) and $\Delta H = -48.6$ kJ M^{-1}. They are identical with the ones obtained by titrating the ligand solution into a solution containing Cs^+ ions (see Table I). If 2:1 complexes were also formed, the values given above should show big discrepancies compared with those in Table I for the reaction of the cryptand (222) and Cs^+.

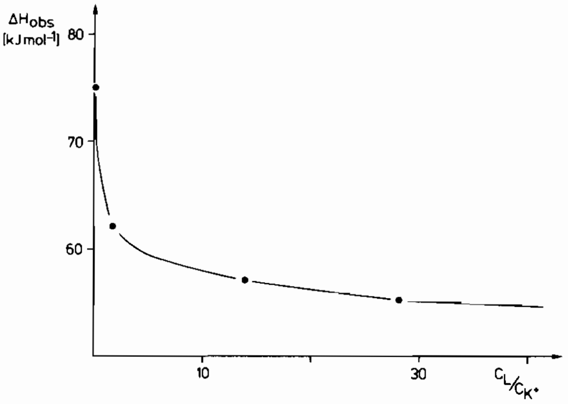

Fig. 3. Observed reaction enthalpies ΔH_{obs} for the calorimetric titrations of solutions containing K^+ and the cryptand (211) at different ratios of ligand to cation concentration with the cryptand (222).

Another experimental set-up was chosen to detect 2:1 complexes of the cryptand (211) with K^+ ions. Solutions of the cryptand (222) were titrated into solutions containing the cryptand (211) and K^+ ions at different ratios of ligand to cation concentrations. The measured reaction enthalpies ΔH_{obs} as a function of this ratio are shown in Fig. 3. Without the ligand (211) one gets the reaction enthalpy ΔH_0 for the reaction of the cryptand (222) with K^+ cations. In cases where only 1:1 complexes between (211) and K^+ are formed and all cations are complexed, the observed reaction enthalpy ΔH_∞ is given by eqn. (2):

$$\Delta H_\infty = \Delta H_0 - \Delta H_L \qquad (2)$$

ΔH_L is the observed reaction enthalpy for the reaction of the ligand (211) with K^+ ions. Even at a seventyfold excess of the cryptand (211) over the K^+ cations, the observed reaction enthalpy ΔH_{obs} is smaller than ΔH_∞. This indicates that the formation of

1:1 complex is not complete at this excess of ligand and no 2:1 complexes have been formed. If both complexes were present, the value of ΔH_{obs} could become smaller than that of ΔH_∞.

From the experimental values of ΔH_0 and ΔH_{obs} it is possible to calculate the stability constant of the complex of the cryptand (211) and K^+ ions. The ratio α of the concentration of the formed complex $[ML^{n+}]$ to the total metal ion concentration c_M can be defined by the following equation:

$$\alpha = \frac{[ML^{n+}]}{c_M} = \frac{\Delta H_0 - \Delta H_{\text{obs}}}{\Delta H_L} \tag{3}$$

Using the mass balances

$$c_M = [M^{n+}] + [ML^{n+}]$$

and

$$c_L = [L] + [ML^{n+}]$$

all concentrations are known, and the stability constant given by eqn. (1) can be calculated. From the experimental reaction enthalpies shown in Fig. 3, a value of $\log K = 2.1 \pm 0.2$ for the stability constant for the reaction of the ligand (211) with K^+ is obtained. The indirectly estimated stability constant is identical with the one measured directly. However, the value is not very accurate due to the low number of datapoints. On the other hand, a big deviation between the directly and indirectly estimated complex stabilities is expected if 2:1 complexes are also present in solution. Thus, in both cases only 1:1 cryptate complexes could be observed in solution.

These experimental results are somewhat surprising, because the existence of 2:1 complexes with crown ethers is well established. However, these results [22] indicate that in most cases the value of the reaction entropy of the second complexation step is more negative than the value for the 1:1 complex formation. In the case of the existence of exclusive complexes with cryptands, the values for the reaction enthalpies are much smaller compared with the values of inclusive complexes. Under the assumption that the reaction enthalpies for both complexes do not differ much, it becomes obvious that entropic contributions can easily overcompensate the enthalpic ones. The formation of 2:1 cryptand complexes is most likely disfavoured by the reaction entropies.

For a detailed discussion of the 1:1 complex formation, several contributions to the observed values of the reaction enthalpies and entropies have to be taken into account. These are: (a) complete or partial desolvation of the cations and ligands, (b) structural changes of the ligands, (c) deformations of the ligands during complexation, and (d) interactions between donor atoms of the ligands and the complexed cations.

The interactions between different solvent molecules and the ligands studied in this work have been measured only for the ligand 18C6 [25]. The estimated stability constants are rather small and the complexation of all cations with this ligand is influenced in the same manner. Therefore, the desolvation of the ligand will not be further discussed with respect to the macrocyclic or cryptate effect because no data are available for ligands – especially noncyclic and bicyclic ligands. In a theoretical study of aqueous solutions of 1,4,7,10-tetraazacyclododecane, the authors came to the conclusion that only one water molecule is located inside the cavity of the ligand. The energy for removing this solvent molecule is very small compared to the energies for binding cations [26]. From experimental findings it is also confirmed that the interactions between solvent molecules and the bicyclic cryptands are weak in comparison with the solvent–cation interactions [27]. By always using the same solvent the influence of the solvating medium can be kept constant in the case of the cations.

Polyethylenglycols as ligands are able to surround a cation completely. The measured reaction enthalpies in this case are related to the desolvation of the complexed cation and the maximum possible interaction between this cation and the donor atoms of the ligands [12]. There exists no possibility to directly estimate the energies for structural changes and deformations of monocyclic or bicyclic ligands. Both energetic contributions account for the differences between the highest values for the reaction enthalpies ΔH_c calculated from the values for the reactions of polyethylenglycols with alkali cations [12] and the measured reaction enthalpies ΔH_m with mono- and bicyclic ligands in methanol. Values of ΔH_c are obtained from the individual bond strengths between alkali cations and ether oxygen donor atoms. Naturally, the number of the replaced solvent molecules has to be taken into account [12]. The results are summarized in Table III.

The smallest deviations $\Delta = \Delta H_c - \Delta H_m$ are found in the case of the ligand 18C6. During the complex

TABLE III. Difference Δ (kJ mol^{-1}) between Calculated and Measured Reaction Enthalpies for Reaction of Alkali Ions with Crown Ethers and Cryptands in Methanol

Ligand	Na^+	K^+	Rb^+	Cs^+
18C6	0	−1	−6	−15
22		−51		
22DD	−17	−24	−16	−36
211	−35	−88	−98	−108
221	−18	−50	−50	−68
222	−28	−36	−33	−65

formation of this ligand with alkali ions, the structural changes and deformation of the crown ether 18C6 are obviously not very significant. However, a small increase of Δ with increasing ionic radii of the complexed cations is observed. These results clearly show that the macrocyclic effect is only caused by favourable entropy changes during the complex formation. No evidence is found for an enthalpic origin of this effect, as was suggested by other authors [28]. The reactions of azacrown ethers with alkali cations display a quite different behaviour. High negative values of Δ are found. As already mentioned, conformational changes of these ligands are responsible for the values of Δ. The *endo–endo* conformation of the ligand (22DD) is preferred due to the long alkyl chains at the nitrogen atoms. The other azacrown ethers have to adapt this conformation during the reactions. These are the main reasons which explain the negative values of Δ calculated for the reactions of the ligands (22) and (22DD).

The molecular structures of cryptands and azacrown ethers are related. Thus, a similar behaviour of Δ can be expected. All values of Δ calculated for cryptands are negative. This means that all measured reaction enthalpies are smaller than the maximal possible values. A distinct trend of the Δ values is evident. If the complexed cation is too big to be completely encapsulated by the cryptand, values of $\Delta \geqslant -50$ kJ mol^{-1} are calculated. For all cations with radii smaller than the cavity diameters, values of $\Delta < -40$ kJ mol^{-1} are obtained. These cations are complexed without any deformations of the cryptands. Thus, only conformational changes of the bicyclic ligands are responsible for the difference between calculated and measured reaction enthalpies.

These results can answer the question of the thermodynamic origin of the 'cryptate effect' in case of the alkali ions. An enthalpic nature of the 'cryptate effect' was reported comparing the data for the reaction of K$^+$ with the cryptand (222) and the monocyclic ligand dicyclohexyl-18-crown-6 [29]. However, in the present study no enthalpic contributions to the 'cryptate effect' could be found. The enormous increase of the stability of cryptand complexes with alkali ions is caused only by favourable entropic changes.

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