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The Macrocyclic and Cryptate Effect.
7. Influence of Structural Changes on the Complexation Behaviour of Aza Crown Ethers and Cryptands in Different Solvents

H.-J. BUSCHMANN

Physikalische Chemie, Universität-GH Siegen, Postfach 101240, D-5900 Siegen, F.R.G.

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Abstract

The complex formation of several mono- and bivalent cations with aza crown ethers, cryptands, and the dilactam analogues of both ligands has been studied in methanol and acetonitrile by means of calorimetric and potentiometric titrations. The complex stabilities of the dilactam ligands are reduced by a factor of more than 10^6 compared with the unsubstituted ligands. This decrease is mainly caused by a strong reduction in the values of the reaction enthalpies. The variation of the mono- and bicyclic ligand structures causes a complete loss of the macrocyclic and cryptate effect.

Introduction

The ability of crown ethers and cryptands to form very stable complexes with different cations is well known [1]. The influence of structural variations of the ligands on the complexation behaviour has been reported in a few cases. The effect of different donor atoms on complex formation reaction has been studied [2–5]. The complexation properties of crown ethers with different mobile side chains have also been reported [6].

In order to obtain monocyclic ligands very easily, crown ether diesters were synthesized [7]. The reactions of a large number of these ligands with different cations in solutions have also been studied [8, 9]. More crown ethers with structural variations can be found in the literature [1]. However, these ligands are not of interest as far as the present study is concerned.

In the case of the cryptands, there are only a few known examples of macrobicyclic ligands with the previously mentioned similar structural changes. The influence of different donor atoms on the reaction of cryptands with cations has been studied [10]. In analogy to the crown ether diesters only two different ligands have been investigated. Due to the chemical nomenclature these macrobicyclic ligands are called dilactams. The stability constants for the reaction of a dilactam cryptand containing the pyridine subcyclic unit with Na^+ and K^+ in aqueous solutions have been published [11]. Stability constants for the complexation of Li^+, Na^+ and Cs^+ by the cryptand(222)–dilactam in several organic solvents have been reported [12].

In order to obtain more information about the complexation behaviour of cryptand dilactams and their monocyclic analogues the reactions of these ligands containing a varying number of donor atoms with different cations was studied in methanol and acetonitrile solutions.

Experimental

All mono- and bicyclic ligands studied in this work, see Fig. 1, are supplied by Merck and used without further purification.

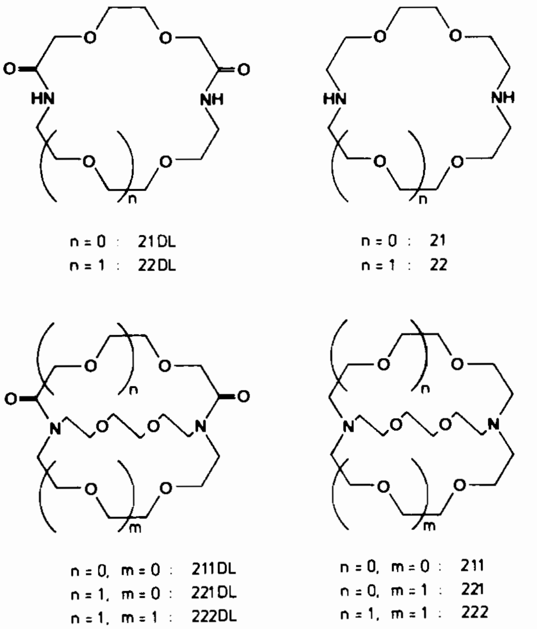

Fig. 1. Ligands studied in this work.

All salts used were of the highest commercial purity available. The tetraphenylborate salts were prepared according to well known procedures [13].

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TABLE I. Stability Constants (log K; K in M^{-1}) and Thermodynamic Parameters (ΔH, $T\Delta S$ in kJ mol^{-1}) for the Reaction of Mono- and Bivalent Cations with Aza Crown Ethers, Cryptands and their Dilactam Analogous in Methanol at 25 °C.

Ligand	value	Na^+	K^+	Rb^+	Cs^+	Ca^{2+}	Sr^{2+}	Ba^{2+}	Ag^+	Pb^{2+}
22	log K	–	1.83^a	$<1^a$	–	3.87^b	5.99^b	6.12^b	10.02^c	9.11^d
	$-\Delta H$		4.7	<2		−5.6	9.0	10.0	44.9	29.1
	$T\Delta S$		5.7			27.6	25.0	24.8	12.0	22.7
22DL	log K	$-^e$	$-^e$	$-^e$	$-^e$	$-^e$	$-^e$	$-^e$	$-^e$	$-^e$
211	log K	6.64^a	2.36^a	2.50^a	2.50^a	5.45^b	2.50^b	2.53^b	10.46^c	9.03^d
	$-\Delta H$	33.1	23.2	8.0	6.5	−2.4	−0.2	−5.5	54.6	24.6
	$T\Delta S$	4.6	−9.8	6.2	7.7	33.4	47.0	30.0	4.8	26.7
211DL	log K	$-^e$	$-^e$	$-^e$	$-^e$	$-^e$	$-^e$	$-^e$	$-^e$	$-^e$
221	log K	9.71^a	8.40^a	7.35^a	4.32^a	$>5^b$	$>5^b$	10.4^b	14.44^c	12.84^d
	$-\Delta H$	49.8	61.1	55.7	47.4	32.5	43.0	38.2	81.9	67.9
	$T\Delta S$	5.4	−13.4	−13.9	−22.9			20.9	0.1	5.1
221DL	log K	$-^e$	$-^e$	$-^e$	$-^e$	3.49	2.98	$-^f$	$-^e$	3.57
	$-\Delta H$					6.0	2.4			5.2
	$T\Delta S$					13.8	14.5			15.1
222	log K	7.97^a	10.49^a	9.10^a	3.95^a	8.16^b	$>5^b$	$>12^b$	12.22^c	12.95^d
	$-\Delta H$	39.8	75.0	72.7	49.7	22.0	42.5	68.9	68.3	72.7
	$T\Delta S$	5.5	−15.4	−21.0	−27.3	24.4			1.1	0.9
222DL	log K	$-^e$	$-^e$	$-^e$	$-^e$	3.58	4.01	2.90	$-^e$	5.39
	$-\Delta H$					18.8	11.8	14.5		17.9
	$T\Delta S$					1.5	11.0	2.0		12.7

[a] From ref. 29. [b] From ref. 30. [c] From ref. 31. [d] From ref. 32. [e] No detectable heat produced during calorimetric titration; log K very small or $\Delta H = 0$. [f] $\Delta H > 0$; no possibility to evaluate K from the thermogram.

Methanol (Merck; H_2O content less than 0.01%) and acetonitrile (Merck; H_2O content less than 0.3%) were used as solvents.

Stability constants smaller than 10^5 and reaction enthalpies were determined using a Tronac Model 450 calorimeter [14].

In order to determine the higher values of the stability constants, ion-selective electrodes for Na^+ (Metrohm EA 109-Na), K^+ (Ingold pK201-S7), Ag^+ (Metrohm EA 282) and Pb^{2+} (Metrohm EA 306-Pb) were used. During the potentiometric titrations the ionic strength was kept constant using tetraethylammonium perchlorate. The reactions observed can be shown by eqn. (1):

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

In cases where no ion-selective electrode for a cation exists disproportionative potentiometric titrations were performed. A solution containing the ligand and a salt is added to a solution containing Na^+, K^+ or Ag^+. From this titration the stability constant for the reaction of the ligand with this salt can be calculated if the stability constant of the complex between the same ligand and Na^+, K^+ or Ag^+ has been estimated separately [15].

The stability constants of the Rb^+ complexes with bicyclic ligands in acetonitrile could only be estimated by this technique without a supporting electrolyte. Otherwise insoluble precipitations were formed.

Results and Discussion

The values of log K, ΔH, and $T\Delta S$ for the complexation reaction of mono- and bivalent cations by aza crown ether dilactams and cryptand dilactams in methanol solutions are summarized in Table I. For comparison the corresponding values of the reactions of the unsubstituted ligands are taken from the literature.

The results obtained in acetonitrile solutions are tabulated in Table II. The already published stability constants for the reaction of the ligand (22) with alkali ions [16], Cs^+ [17], and Ag^+ [18, 19] and of the ligand (21) with Ag^+ [19] are very much in agreement with our data. Also, positive agreement between

TABLE II. Stability Constants (log K; K in M^{-1}) and Thermodynamic Parameters (ΔH, $T\Delta S$ in kJ mol^{-1}) for the Reaction of Mono- and Bivalent Cations with Aza Crown Ethers, Cryptands and their Dilactam Analogous in Acetonitrile at 25 °C

Ligand	value	Na^+	K^+	Rb^+	Cs^+	Ba^{2+}	Ag^+
21	log K	–[a]	2.11	–[a]	–[a]	>6.5	6.55
	$-\Delta H$		10.8			35.0	31.7
	$T\Delta S$		1.2				5.5
21DL	log K	–[a]	–[a]	–[a]	–[a]	–[a]	–[a]
22	log K	3.92	4.13	3.32	2.69	>8	7.93
	$-\Delta H$	3.6	15.3	10.1	6.0	54.7	30.5
	$T\Delta S$	18.7	8.2	8.8	9.3		14.6
22DL	log K	–a	–[a]	–[a]	–[a]	3.89	–[a]
	$-\Delta H$					9.3	
	$T\Delta S$					12.8	
211	log K	8.74	3.50	3.9	–[a]	6.32	7.74
	$-\Delta H$	52.9	29.3	9.5		32.4	47.5
	$T\Delta S$	–3.2	–9.4	12.7		3.5	–3.5
211DL	log K	–[a]	–[a]	–[a]	–[a]	–[a]	–[a]
221	log K	10.97	9.10	6.74	4.68	>11	11.29
	$-\Delta H$	65.5	64.1	56.3	45.8	78.3	62.7
	$T\Delta S$	–3.2	–12.4	–18.0	–19.2		1.4
221DL	log K	4.24	–[a]	–[a]	–[a]	>5	–[a]
	$-\Delta H$	3.3				36.7	
	$T\Delta S$	20.8					
222	log K	10.68	9.56	9.65	4.83	>9	8.94
	$-\Delta H$	61.9	74.0	71.6	44.2	108.8	52.3
	$T\Delta S$	–1.2	–19.7	–16.8	–16.8		–1.5
222DL	log K	3.96	2.20	2.32	–[a]	>5	–[a]
	$-\Delta H$	17.9	18.3	4.2		32.2	
	$T\Delta S$	4.6	–5.8	9.0			

[a] No detectable heat produced during calorimetric titration; log K very small or $\Delta H = 0$.

stability constants from the literature and values measured for the complex formation of the cryptand (211) with K^+ [20] and Ag^+ [21], the cryptand (221) with Ag^+ [19] and the cryptand (222) with Na^+, K^+, Rb^+, Cs^+ and Ag^+ [20, 22] can be found. The published stability constant and reaction enthalpy for the complexation of Na^+ by the ligand (211) is almost identical with our values [23]. For the reaction of (222DL) with Na^+ in acetonitrile solution only a lower limit of the stability constant is known [12].

Due to both carbonyl groups in the dilactam ligands the nitrogen donor atoms should be less basic compared with the unsubstituted ligands. This can easily be shown for the diprotonation of the cryptands (222) and (222DL) in methanol. The measured reaction enthalpies are $\Delta H = -112.0$ kJ mol^{-1} in the case of (222) and $\Delta H = -3.0$ kJ mol^{-1} in the case of (222DL). The carbonyl groups also increase the rigidity of the ligands. The possibility of adapting different conformational forms is therefore reduced.

Both effects may account for the drastic decrease in stability of the complexes formed with the substituted ligands in methanol solutions. The measured stability constants of the dilactam ligands are reduced by a factor of 10^5 up to 10^{10} compared with the unsubstituted ligands. Therefore, in a few cases only, a reaction between the cryptand–dilactams and cations is observable. Between the dilactam ligands and alkali ions and the silver ion no reaction could be detected by means of calorimetric and potentiometric titrations. Only the divalent cations are able to form complexes with the substituted ligands.

To discuss these observations in more detail it is necessary to compare the thermodynamic data for the reactions of the substituted and unsubstituted ligands. All measured values of the reaction enthalpies of the dilactam ligands in methanol solutions are lower in comparison with the values of the unsubstituted ligands. The differences are however in the range from 60 to 3 kJ mol^{-1}. The smallest difference is obtained for the complexation of Ca^{2+} by the ligand (222) and (222DL). In this case the cavity diameter is much larger [24] than the ionic radius of Ca^{2+} [25]. Under these circumstances no optimal interaction between all donor atoms and the complexed cations seems to be possible.

Besides the reduction in the complex stabilities of the dilactam ligands due to enthalpic contributions the reaction entropies also play an important role. Due to the lower structural flexibility of the substituted ligands the values of the reaction entropies also disfavour the complex formation with the dilactam ligands. However, the enthalpic term plays the most important role.

In order to get more experimental details about the reaction of the dilactam ligands with cations, the measurements were also carried out in acetonitrile solutions. Gutmann's donor number of acetonitrile ($DN = 14.1$) is nearly half of the value found for methanol ($DN = 30.2$) [26]. Thus, one may expect that solvation effects upon the cations are reduced during the complex formation. However, strong partly covalent interactions between the silver ion and acetonitrile have been reported [27]. Therefore, the stability constants of all silver complexes are lower in comparison with the values of the reaction in methanol solutions. As expected this effect is mainly caused by enthalpic factors.

Higher values for the stability constants of the other cations in acetonitrile are found. These are due to an increase in the values of the reaction enthalpies. Thus, the observation of diaza crown ether complexes with alkali ions in solution becomes possible. The measured stability constants show, however, a less pronounced selectivity pattern as was found in the reaction between alkali ions and 18-crown-6 in methanol solutions [28].

A similar situation is found in the reactions of cryptands with alkali ions. The stability of the complexes formed increases and in contrast the selectivity of a cryptand against different cations is reduced. If the cations are too large to be encapsulated completely the values of the reaction enthalpies and entropies become very similar in both solvents.

As already observed with methanol solutions, the complex stabilities of the dilactam ligands are reduced by a factor of more than 10^6 compared with the unsubstituted ligands. The decrease in complex stabilities is caused by a strong reduction in the values of the reaction enthalpies. Therefore, only the reaction between Ba^{2+} and (22DL) is measurable.

Some important conclusions can be drawn from the experimental results of the bicyclic ligands. The differences between the measured reaction enthalpies for the reactions of the ligands (222) and (222DL) with alkali ions depend on the radii of the complexed cations. They become larger with increasing cation size. The same situation is also found in the reactions of both ligands with alkaline-earth cations in methanol solutions. During the complex formation process of the less flexible dilactam ligand with the smallest cations measured this handicap is not as important as it is when the larger cations are concerned. This advantage disappears if the cavity of the ligand is reduced. The difference between the reaction enthalpies for the reaction between the ligands (221) and (221DL) with Na^+ in acetonitrile and with Ca^{2+} in methanol is of the same magnitude as it is in the reactions of (222) and (222DL) with larger cations.

As far as the values of the reaction entropy are obtainable, they indicate that the complex formation with dilactam ligands is favoured by convenient entropy changes when compared with the unsubstituted cryptands.

In contrast, the reaction entropy disfavours the formation of dilactam complexes with alkaline-earth cations in methanol solutions. Due to the fact that the stability of the barium complexes in acetonitrile was too high to be estimated by means of the experimental methods used no statement can be made.

However, the dominant factor of the differences observed in the complexation behaviour between cryptands and dilactam cryptands remains the change in the reaction enthalpies.

The reduced ligand flexibility and the reduction in the electron density of the donor atoms located beside both carbonyl groups is mainly responsible for the observed complexation behaviour of the dilactam ligands. This variation of the mono- and bicyclic ligand structures cause a complete loss of the so-called macrocyclic and cryptate effect.

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