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The Macrocyclic and Cryptate Effect.
3. Complexation of Barium(II) by Monocyclic and Bicyclic Ligands in Methanol

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Abstract

The complexation of Ba^{2+} by different crown ethers, azacrown ethers and cryptands was studied in methanol by calorimetric and potentiometric titrations. A macrocyclic effect was found for the reactions of crown ethers, caused by favourable entropic changes. Azacrown ethers exist in different conformational forms. The energy for the nitrogen inversion which takes place when the conformation changes was calculated using the estimated Ba^{2+}–O bond strength. The bicyclic ligand (211) is too small to form a real inclusion compound. This is possible with the larger bicyclic ligands (221) and (222). A big rise in complex stability with these ligands is observed. The cryptate effect is mainly due to an increase in reaction enthalpies.

Introduction

Crown ethers and cryptands complex alkali and alkaline-earth cations very strongly. Additionally these ligands show a pronounced selectivity. The high stability constants of crown ether complexes have been explained by a 'macrocyclic effect' [1]. In analogy a 'cryptate effect' was proposed to explain a further increase in complex stability of the cryptands [2]. Very few experimental data are known to verify these two effects [3]. Their interpretation leads to contradicting conclusions.

In recent publications we reported the complexation of Pb^{2+} [4] and Ag^{+} [5] by noncyclic, monocyclic, and bicyclic ligands. Both cations show strong interactions with nitrogen donor atoms and much smaller ones with oxygen donor atoms. It was found that the macrocyclic effect is only of entropic origin and the cryptate effect mainly of enthalpic origin. The reactions of azacrown ethers and cryptands are accompanied by conformational changes of the ligands. The energy loss for the nitrogen inversion which takes place during complexation is partly compensated by the strong interactions of the nitrogen atom with Pb^{2+} and Ag^{+}. Thus it seemed worthwhile to investigate the complex formation of these ligands with Ba^{2+}. This cation does not show detectable interactions with nitrogen atoms.

Experimental

The monocyclic and bicyclic ligands examined in this work are shown in Fig. 1. All samples are commercially available (Merck) and were used without further purification. Solutions of $Ba(ClO_4)_2$ (Merck) were prepared by dissolving the anhydrous salt in methanol (H_2O content less than 0.01%; Merck).

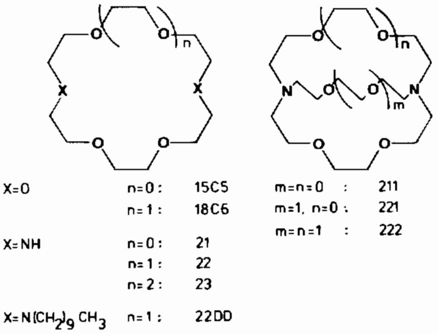

Fig. 1. Mono- and bicyclic ligands studied.

Stability constants smaller than 10^5 were estimated from calorimetric titration data using a Tronac Model 450 calorimeter. The method has been described elsewhere [4]. Stability constants higher than 10^5 were measured by calorimetric (a) or potentiometric (b) competition titrations:

(a) in the course of the calorimetric competition titration the heat of reaction (1) was measured:

$$Ba^{2+} + [LM]^{n+} \rightleftharpoons [LBa]^{2+} + M^{n+} \qquad (1)$$

where L is a ligand molecule and M^{n+} a cation. The stability constant and reaction enthalpy for reaction (1) is calculated from the thermogram. By combination with the separate estimated value for the stability of the $[LM]^{n+}$-complex one gets the stability constant of the corresponding barium complex. The

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TABLE I. Stability Constants (log K; K in M^{-1}) and Thermodynamic Parameters for the Reaction of Ba^{2+} with Mono- and Bicyclic Ligands in Methanol at 25 °C.

Ligand	log K	$-\Delta H$ [kJ mol^{-1}]	$T\Delta S$ [kJ mol^{-1}]
15C5[a]	4.09	20.9	2.3
18C6	7.38[b]	48.5	−6.5
21C7[c]	5.44	28.5	2.5
21	2.72	−4.1	19.6
22	6.12[b]	10.0	24.8
22DD	5.84[b], 5.79[d]	32.9	0.3
23	5.39[d]	8.5	22.1
211	2.53	5.5	8.9
221	10.4	38.2	20.9
222	>12.2	68.9	

[a] From ref. [19]. [b] From a calorimetric competition reaction. [c] From ref. [8]. [d] From a potentiometric competition reaction.

method will be described in detail in another publication [6]. The slow dissociation of complexes with bicyclic ligands prevents the estimation of any value from the thermogram.

(b) during the potentiometric competition reaction (2):

$$[LBa]^{2+} + Ag^{+} \rightleftharpoons [LAg]^{+} + Ba^{2+} \qquad (2)$$

the barium complex was added to a solution of $AgNO_3$. The concentration of the free silver ions was monitored by means of a silver electrode (Metrohm EA 282). Using the stability constants of the silver complexes [5] the stabilities of the Ba^{2+} complexes can also be calculated.

For the reaction of $[222\ Ba]^{2+}$ with Ag^+ no exchange of the cations was observed, even after 20 h reaction time. The ionic strength was 5×10^{-2} M, and $N(C_2H_5)_4ClO_4$ or $N(C_2H_5)_4NO_3$ was used as supporting electrolyte. The detailed experimental procedure is described in [7]. A potentiometric estimation of the stability of the $[Ba\text{-}22]^{2+}$ complex was not possible. Insoluble precipitations were formed even when the concentrations were varied and no supporting electrolyte was used.

Results and Discussion

The values of the stability constants, reaction enthalpies, and entropies for the complexation of Ba^{2+} by mono- and bicyclic ligands are summarized in Table I. The published complex stability and thermodynamic values for the reaction with 18C6 [8] and (22) [9], and the stability constant of the complex with (221) [10], agree very well with our data.

Stability constants and reaction enthalpies of Ba^{2+} with a great number of noncyclic ligands have already been measured and published [11]. The reaction enthalpies of glycols, $H(OCH_2CH_2OCH_2CH_2)_mOH$, and glymes, $CH_3(OCH_2CH_2OCH_2CH_2)_mOCH_3$, show a linear dependence with the number of ether oxygen atoms in the ligand, see Fig. 2. The slopes of both straight lines provide a medium bond strength of 9.1 ± 0.2 kJ mol^{-1} for a single Ba^{2+}–O bond.

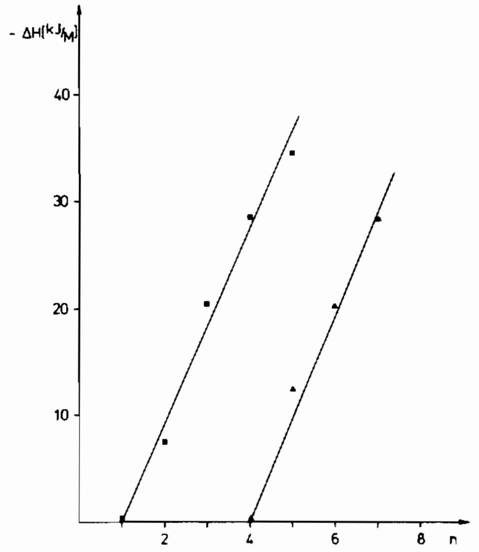

Fig. 2. The measured reaction enthalpies for the complexation of barium by glycols, $H(OCH_2CH_2OCH_2CH_2)_mOH$ (■), and glymes, $CH_3(OCH_2CH_2OCH_2CH)_mOCH_3$ (▲) as a function of the number of ether oxygen atoms in the ligand.

The complex with the monocyclic ligand 15C5 is not significantly more stable in comparison with the analogous noncyclic glycol [11]. For the reaction enthalpy with 15C5 we obtain a value which is more than 10 kJ mol^{-1} less negative than in the case of the glycol. The cavity of 15C5 (r = 0.9 Å) [12] is too small to accommodate the barium ion (r = 1.36 Å [13]. In the monocyclic ligand 15C5 there are not sufficient donor atoms able to interact with Ba^{2+}, whereas the flexible noncyclic ligand can wrap itself around the cation. In contrast the cavity of 21C7 (r = 1.9 Å) [12] is too large. The barium ion fits best into the cavity of 18C6 ($r = 1.4$ Å) [12], allowing optimum interaction between the complexed cation and the donor atoms of the ligand. Indeed the values for the stability constant and reaction enthalpy are much higher compared with those of 15C5. Under the assumption of equal bond strength one only gets 8.1 kJ mol^{-1} for the strength of a single Ba–O bond. This value is 1 kJ mol^{-1} smaller than that determined from the reaction enthalpies of noncyclic ligands. Two different reasons may be responsible for this observation:

(a) during complexation the ligand has to undergo conformational changes;

(b) not all donor atoms of 18C6 interact with Ba^{2+}.

To (a): it is known that 18C6 exists in two conformers. Ultrasonic relaxation techniques were used to measure the kinetics of the conformational change, the equilibrium constant and the reaction enthalpy [14]. From the equilibrium constant it can be concluded that one conformational form is predominant. If only this form reacts with cations the decrease of the measured reaction enthalpy for complexation should be very small. In fact, this was found for the complex formation to be between 18C6 and Ag^+ [5], so that the second argument seems to be more relevant. The radius of the cavity of 18C6 is only 0.06 Å greater than the radius of the barium ion. This may cause an asymmetric arrangement where the cation is displaced from the mean plane of the oxygens leading to different $Ba^{2+}\cdots O$ distances. A similar situation was found for the complex between 18C6 and Rb^+, where the cation radius is 0.08 Å greater than the ligand [15].

It is obvious that a macrocyclic effect exists for the complexation of Ba^{2+}. From the experimental results it may be concluded that this effect is only caused by favourable entropic changes.

The complex formation of barium ions with azacrown ethers is more difficult to interpret. All measured reaction enthalpies of these ligands are smaller compared with the corresponding crown ethers. For the complexation of Ba^{2+} by (21) even a positive reaction enthalpy is measured. The complex formation with (22) and (23) also produces small values for the reaction enthalpies. Like the crown ethers, complexation is only favoured by the reaction entropy but is disadvantaged by the reaction enthalpy. As a result all stability constants of azacrown ethers are smaller than with crown ethers.

A great increase of the reaction enthalpy is found for the ligand (22DD) accompanied by an opposite change of the reaction entropy. It is known that azacrown ethers exist in different conformational forms such as cryptands [16], see Fig. 3. Obviously, substituting the protons of the amino groups of (22) with long alkyl chains shifts the equilibrium to the endo-endo conformation.

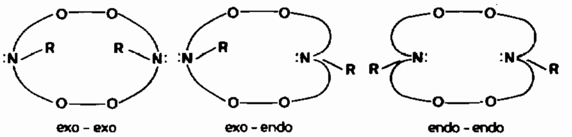

Fig. 3. Different conformational forms of uncomplexed azacrowns.

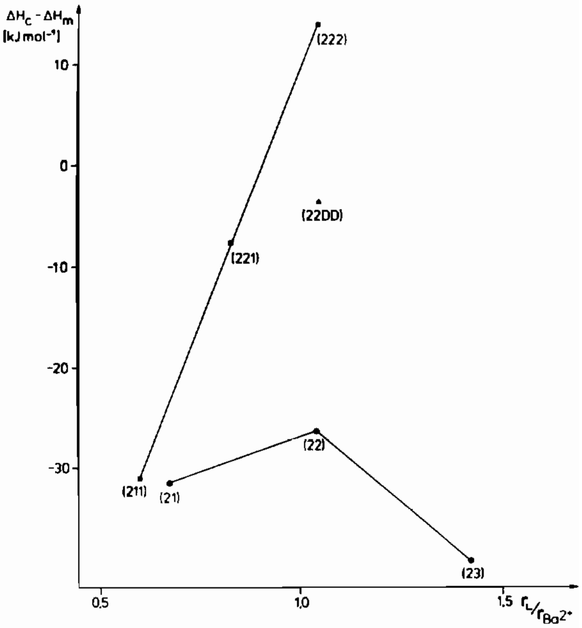

Fig. 4. Difference between calculated (ΔH_c) and measured reaction enthalpies (ΔH_m) as a function of the ligand-to-barium radii.

Under the assumption that no interaction between Ba^{2+} and nitrogen atoms take place it is possible to calculate reaction enthalpies for the complex formation with azacrown ethers. The results are shown in Fig. 4. The measured reaction enthalpies for the ligands (21) and (22) are about 30 kJ mol^{-1} smaller than the calculated values. The same was found for the complexation of Ag^+ with these ligands [6]. The difference can be attributed to the inversion of the two nitrogen atoms of the monocyclic ligands. Since (22DD) mainly exists in one conformation the measured reaction enthalpy is only 4 kJ mol^{-1} smaller than the calculated value. The ligand (23) is too large ($r = 1.9$ Å) [12] for the barium ion. In order to get optimum interactions between the cation and most oxygen donor atoms of (23) the ligand has to adapt a distorted conformation. This leads to a greater difference between calculated and measured values for the reaction enthalpy.

The stability of the barium complex with the bicyclic ligand (211) is very similar to that of (21). The cavity of (211) ($r = 0.8$ Å) [17] is much too small to accommodate Ba^{2+}. No real inclusion compound can be formed as it was observed for the reaction between (222) and Cs^+ [18]. With increasing cavity size a great enhancement of the complex stability of (221) ($r = 1.1$ Å) and (222) ($r = 1.4$ Å) [17] is found. The difference between calculated and measured reaction enthalpy of (221) is nearly zero, see Fig. 4. The reaction of (222) with Ba^{2+} even leads to a positive difference. The energy for the nitrogen inversion is still taken away from the measured reaction enthalpies. Only stronger interactions between the complexed ion and the donor atoms can account for this.

The complexation of Ba^{2+} by cryptands is a further example of how the cryptate effect can be explained essentially by favourable enthalpic changes.

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