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The Macrocyclic and Cryptate Effect.
8. Complex Formation of the Cryptands (222), (222B), (222BB) and (222CC) with Different Cations in Methanol Solutions

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Abstract

The complexation reactions between the cryptands (222), (222B), (222BB) and (222CC) with mono- and bivalent cations in methanol solutions were studied by means of potentiometric and calorimetric methods. Stability constants and reactions enthalpies for the complexation of monovalent cations by the ligands (222), (222B) and (222BB) are almost constant. However, large reductions in the complex stabilities of bivalent cations with these ligands can be observed. Only enthalpic factors cause these reductions. Differences between cations are responsible for these observations. A reduction in the values of the reaction enthalpy measured is found with all cations on comparison with all other macrobicyclic ligands in the case of the ligand (222CC).

Introduction

Since the discovery of macrobiocyclic ligands (cryptands) [1] and of the ability of these ligands to form very stable complexes with cations [2] by Lehn and his co-workers, there has been a considerable number of experimental results dealing with the complex formation [3].

Structural variations at the cryptand molecule are able to vary their complexation abilities considerably. The replacement of one or more of the oxygen donor atoms by nitrogen atoms causes a decrease in the alkali and alkaline-earth complex stabilities. On the other hand, the stability of complexes formed with transition metal ions increases [4]. Other structural changes in the cryptand molecules reduce the complex stability with all cations examined in solution [5]. For example, the complexes formed with dilactam cryptands are more than a factor of 10^5 less stable when compared with the unsubstituted ligands [6].

The benzene rings of the cryptands (222B) and (222BB) are also expected to influence the complexation behaviour of these ligands. Thus, the basicity of oxygen donor atoms next to the benzene rings is reduced, the flexibility of these ligands is smaller in comparison with the unsubstituted cryptands, and any other differences may also influence their complexation behaviour. Only small changes in the complex stabilities between (222), (222B) and (222BB) have been reported for alkali cations [7, 8]. Enthalpic and entropic factors are responsible for these observations.

A reduction in the complex stabilities of several orders of magnitude are known for other cations [3]. In these case no values for the reaction enthalpy and entropy have been published. Thus, a decision about the factors for the complex stability reduction is not possible.

Therefore, as a continuation of earlier works about the influence on the macrocyclic and cryptate effect [6], a study was made of the reactions between mono- and bivalent cations and the different cryptands.

Experimental

The macrobicyclic ligands studied, see Fig. 1, were supplied by Merck and used without further purification. The following anhydrous salts: $NaNO_3$ (Merck), KJ (Merck), RbJ (Merck), $RbNO_3$ (Merck), CsF (Ventron), $AgNO_3$ (Merck), $Ca(NO_3)_2$ (BDH), $Sr(NO_3)_2$ (Ventron) and $Ba(ClO_4)_2$ (Merck) were dried under vacuum. Methanol (Merck; H_2O content less than 0.01%) was used as the solvent.

Stability constants smaller than 10^5 M^{-1} and all reaction enthalpies were determined using a Tronac Model 450 calorimeter. The evaluation of the measured thermograms has already been described in detail [9].

Direct potentiometric titrations with ion-selective electrodes were performed to obtain the complex stabilities with Na^+ (Metrohm EA 109-Na), K^+ (Ingold pK 201-S7), and Ag^+ (Metrohm ES 282). The reactions observed are given by eqn. (1):

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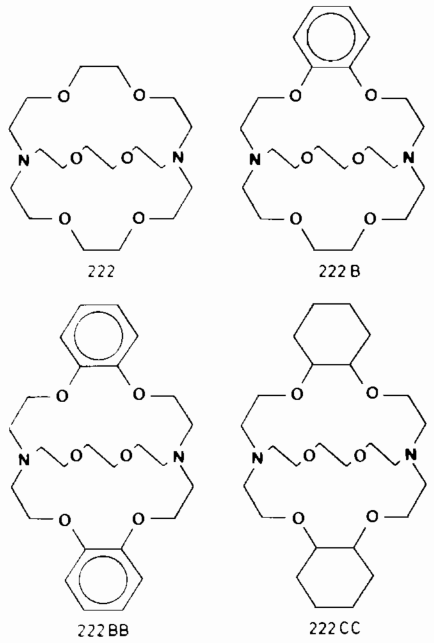

222 222B 222BB 222CC

Fig. 1. Ligands studied in this work.

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

The remaining stability constants were measured using disproportionate potentiometric titrations with Ag^+ [10]. In this case the reaction shown in eqn. (2) takes place:

$$ML^{n+} + Ag^+ \rightleftharpoons AgL^+ + M^{n+} \qquad (2)$$

$$\text{with } K' = \frac{[AgL^+][M^{n+}]}{[ML^{n+}][Ag^+]}$$

With the separate estimated stability constant of the silver complex (K_{ag}) it is possible to calculate the unknown value of K from the measured value of K':

$$K = \frac{K_{Ag}}{K'}$$

During all potentiometric titrations the ionic strength was 5×10^{-2} M, and $N(C_2H_5)_4ClO_4$ (Fluka) or $N(C_2H_5)_4NO_3$ (Fluka) was used as the supporting electrolyte. Under experimental conditions, insoluble precipitations formed between Ba^{2+} and the cryptand (222BB) even without the supporting electrolyte.

Results and Discussion

The values of $\log K$, ΔH, and $T\Delta S$ for the complexation of monovalent cations by different cryptands are summarized in Table I. The results obtained with bivalent cations are tabulated in Table II. The stability constants already published for the reaction of the cryptands (222B) and (222BB) with alkaline-earth cations [11, 12] are very much in agreement with our data. So far, no data for the reaction of the ligand (222CC) have been published to enable comparison.

The most stable complex of the cryptand (222) and alkali ions is formed with K^+. This cation (r = 1.38 Å, [13]) fits optimally into the ligand cavity (r = 1.4 Å, [14]). For other cations with cavity dimensions smaller than these, the interactions between the complexed cations and all donor atoms are reduced. Cations that are too big for the cavity deform the ligand. In extreme cases, the formation of exclusive complexes is possible [15].

These effects are mainly responsible for the reaction enthalpies observed. Solvation effects of the

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 Different Cryptands with Monovalent Cations in Methanol at 25 °C

Ligand	Value	Li^+	Na^+	K^+	Rb^+	Cs^+	Ag^+
222	$\log K$	2.46[a]	7.97[a]	10.49[a]	9.10[a]	3.95[a]	12.22[b]
	$-\Delta H$	3.7[a]	39.8[a]	75.0[a]	72.7[a]	49.7[a]	68.3[b]
	$T\Delta S$	10.3[a]	5.5[a]	−15.4[a]	−21.0[a]	−27.3[a]	1.1[b]
222B	$\log K$	2.19[c]	7.50[c]	9.21[c]	7.19[c]	2.99[c]	11.98[d]
	$-\Delta H$		39.7[c]	65.3[c]	57.7[c]	31.8[c]	65.1[d]
	$T\Delta S$		2.9[c]	−13.0[c]	−16.8[c]	14.8[c]	3.0[d]
222BB	$\log K$	2.0[e]	7.60[e]	8.74[e]	5.91[e]	2.61[e]	11.84[d]
	$-\Delta H$		42.5[e]	66.2[e]	53.7[e]	38.5[e]	65.4[d]
	$T\Delta S$		0.7[e]	−16.5[e]	−20.1[e]	−23.7[e]	1.9[d]
222CC	$\log K$		6.02	6.92	5.65	2.55	12.39[d]
	$-\Delta H$		27.4	36.1	34.3	3.3	61.4[d]
	$T\Delta S$		6.8	3.2	−2.2	11.2	9.0[d]

[a] From ref. 23. [b] From ref. 24. [c] From ref. 7. [d] From ref. 25. [e] From ref. 8.

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 Different Cryptands with Bivalent Cations in Methanol at 25 °C

Ligand	Value	Ca^{2+}	Sr^{2+}	Ba^{2+}	Pb^{2+}
222	log K	8.16[a]	11.75[b]	12.9[c]	12.95[d]
	$-\Delta H$	22.0[a]	42.5[a]	68.9[a]	72.7[d]
	$T\Delta S$	24.4[a]	24.3[a]	4.4[a]	0.9[d]
222B	log K	7.04	10.32	10.99	12.22[d]
	$-\Delta H$	17.7	34.3	53.9	61.2[d]
	$T\Delta S$	22.3	24.3	8.5	8.2[d]
222BB	log K	5.96	8.83	8.85[b]	10.90[d]
	$-\Delta H$	6.4	25.9	33.5	52.7[d]
	$T\Delta S$	27.5	24.3	16.8	9.2[d]
222CC	log K	5.12	8.59	9.75	11.55[d]
	$-\Delta H$	<1	5.4	35.5	48.4[d]
	$T\Delta S$		43.4	19.9	17.2[d]

[a] From ref. 26. [b] From ref. 11. [c] From ref. 12. [d] From ref. 27.

cations partly account for the reaction entropies. The stronger the solvation of the cation, the more solvent molecules are liberated during the complexation reaction. As a result, the values of the reaction entropies decrease evenly from Li^+ to Cs^+. The same explanation is valid for the complex formation of the ligand (222) with alkaline-earth cations. Additional contributions to the reaction enthalpy and entropy are very probable, e.g. changes in the cation and ligand solvation, reduction of the ligands flexibility and so on. However, some of these effects can be assumed to be almost constant in a given solvent. The interactions between alkali and alkaline-earth cation and solvent molecules or ligand donor atoms are mainly of electrostatic nature. In the case of Ag^+ and Pb^{2+} one expects a covalent character in the bonds formed with nitrogen donor atoms. As a result both cations show strong interactions with these donor atoms [16].

The benzene rings in the cryptands (222B) and (222BB) reduce the cavity sizes of the ligands, as the distance between the oxygen atoms bonded with the benzene rings are smaller than in the unsubstituted cryptand. Further, the basicity of the oxygen donor atoms next to the benzene rings is reduced, and the rigidity of the ligands is increased. The results from the monovalent cations, Table I, demonstrate the influence of changes in the ligand structure.

If the cation diameter is smaller in comparison with the cavity diameter, only a minor reduction in the stability constant and no effect on the reaction enthalpy is observed. This applies to Li^+, Na^+, and Ag^+. The decrease in cavity size and the reduction in conformational flexibility leads to a much smaller stability constant for the bigger alkali ions (K^+, Rb^+, and Cs^+). Both enthalpic and entropic contributions are responsible. The reaction enthalpies for the reaction of the cryptands (222B) and (222BB) with monovalent cations are almost constant. They are obviously not affected by the second benzo group of the ligand. Further reduction in the stability constants is only due to entropic changes.

A completely different situation is found in the complexation of bivalent cations. The stability constants decrease from the ligand (222) to (222B) and to (222BB). This uniform decay is caused by unfavourable enthalpic changes. The values of the reaction entropy remain constant, whereas an increase even favours the complexation reaction.

The differences already mentioned in the chemical behaviour between the cryptand (222) and its benzo substituted analogues should however be valid for the bivalent cations, too. Obviously further factors have to be taken into account. The differences between the complexation of mono- and bivalent cations by the cryptands used can only arise from solvation effects of the cations.

X-ray diffraction studies of aqueous alkali-halide solutions show a very weak second solvation shell [17]. It is also found that the chemical shift of the lithium ion complexed by the cryptand (211) is independent of the solvent [18]. These experimental results indicate that no interactions between complexed monovalent cations and additional solvent molecules take place. On the other hand, the existence of a second solvation shell is confirmed by X-ray diffraction studies of aqueous alkaline-earth chloride solutions [19]. Interactions between divalent cations complexed by the ligand (222) and solvent molecules are concluded from experimental volumes of complexation [20]. The benzo groups of the cryptands (222B) and (222BB) therefore increase the distance between the complexed cation and the second solvation shell. As a result, the values of the reaction enthalpy observed decrease. However, during the complexation of bivalent cations by the macrobicyclic ligands more solvent molecules from the first and second solvation are liberated compared with the monovalent cations.

More insight into the reactions taking place is only possible for the complexation of K^+ and Ba^{2+} since both cations are almost identical in size [13]. In the case of the other cations individual changes in the conformation of the ligand cannot be excluded in order to achieve optimum interaction between the complexed cation and all donor atoms. If only ion–dipole interactions have to be taken into account the process of desolvating and establishing new interactions with the ligand donor atoms for K^+ and Ba^{2+} should be independent of the charge of the cations. The reaction enthalpies measured for the reaction of the ligand (222) are therefore very similar. Entropic factors are responsible for the difference in both stability constants.

The difference of the $T\Delta S$ values of both cations at 25 °C is as follows:

$$T\Delta S_{\mathrm{Ba}^{2+}} - T\Delta S_{\mathrm{K}^+} = 19.9 \qquad (\mathrm{kJ\ mol^{-1}})$$

The entropy of fusion for methanol is estimated to be 18.0 J K^{-1} mol^{-1} [21]. Using both values it is possible to calculate the difference in the number of liberated solvent molecules during the complex formation of both cations. These results indicate that a further four solvent molecules are set free during the complexation of Ba^{2+} compared with K^+. These findings are in accordance with the differences in the solvation number of both cations [22].

The reaction entropies measured for the complexation of K^+ and Ba^{2+} by the ligand (222B) indicate that the difference in the number of solvent molecules set free during the reaction is the same as that found for the ligand (222). One benzo group obviously does not disturb the second solvation shell of Ba^{2+}. Therefore, the same reasons already discussed for the monovalent cations are responsible for the reduction in the complex stability of the bivalent cations.

The reaction entropy differences in the reaction of the ligand (222BB) with K^+ and Ba^{2+} show evidence for the perturbation of the second solvation sphere around Ba^{2+}. One can calculate that 6 further solvent molecules from Ba^{2+} compared with K^+ are liberated during the complexation. The second benzo group avoid any further contact between the complexed Ba^{2+} and additional solvent molecules.

The explanation of the stability constants observed and the thermodynamic values for the reaction of the cryptand (222CC) with mono- and bivalent cations is very difficult. The basicity of all donor atoms should be similar to the unsubstituted ligand (222). The flexibility of this cryptand should be between that of (222) and (222BB). However, the second solvation shell of bivalent cations should also be disturbed by the spacious cyclohexano groups of the ligand. Surprisingly, one finds values for the reaction enthalpy showing an increased reduction for all cations, with the exception of Ba^{2+}, in comparison with the results for (222BB). On the other hand, the complex formation with the ligand (222CC) is generally favoured by entropic contributions.

All these results clearly demonstrate the influence of structural changes on the complex formation with macrobicyclic ligands. The influence of a second solvation shell is expected to diminish in solvents with lower solvating abilities. Unfortunately, no data are available to verify the given explanations by comparison with the results for other solvents.

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