Thermochimica Acta, 211 (1992) 13–20
Elsevier Science Publishers B.V., Amsterdam

Complexation of alkaline earth (Group 2A) cations by non-cyclic, macrocyclic, and macrobicyclic ligands in propylene carbonate solutions

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(Received 3 April 1992)

Abstract

Stability constants and thermodynamic parameters for the reaction of non-cyclic polyethers, crown ethers and cryptands with alkaline earth cations in propylene carbonate were measured by means of calorimetric, potentiometric and conductometric titrations. A linear correlation between the number of oxygen donor atoms of the non-cyclic polyethers and the values of the reaction enthalpies is found. From these data, mean interaction energies between one cation and one donor atom can be calculated. These values can be used to predict the values of the reaction enthalpies of crown ethers with these cations in propylene carbonate. If the cation dimensions are smaller than or equal to the cavity dimensions, the agreement between the calculated and experimentally measured reaction enthalpies is very good, indicating that the macrocyclic effect for these ligands and cations is caused only by entropic contributions.

INTRODUCTION

More than twenty years ago, the complexation abilities of macrocyclic polyethers were discovered by Pedersen [1]. Only two years later, the first macrobicyclic ligands were synthesized by Dietrich et al. [2]. In the meantime, the number of papers dealing with crown ethers and cryptands increases from year to year. However, the many factors influencing the stabilities of the complexes formed are not yet well understood [3, 4]. Sometimes the origins of the macrocyclic and cryptate effects seem to result from enthalpic contributions and, in other cases, from entropic contributions. A more or less consistent interpretation of all known results for the complex formation of non-cyclic polyethers, crown ethers and cryptands with cations in methanolic solution has been made [5]. The known experimental data in this solvent indicate that the macrocyclic and

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perhaps also the macrobicyclic effect are caused mainly by entropic contributions, as for the chelate effect.

However, up to now it is not clear whether or not this interpretation is valid for other solvents too. Therefore a continuation of our earlier works seems to be worthwhile [6]. A reduction of the cation–solvent interactions is expected to result in an increase in the stability constants, mainly due to enthalpic contributions. Therefore the aprotic solvent propylene carbonate was chosen in which, due to its high dielectric constant, many salts are readily soluble and dissociate completely. Thus, no problems due to ion-pair formation occur.

EXPERIMENTAL

The following non-cyclic ligands were used: 2,5,8-trioxanonane (DG, Riedel-de Haen), 2,5,8,11-tetraoxadodecane (TG, Merck), 2,5,8,11,14-pentaoxapentadecane (TeG, Riedel-de Haen), 2,5,8,11,14,17-hexaoxaoctadecane (PG, Riedel-de Haen) and 2,5,8,11,14,17,20-heptaoxaheneicosane (HG, Riedel–de Haen). If the purity of these ligands was not high enough, they were distilled under reduced pressure prior to use.

The macrocyclic and macrobicyclic ligands were commercial samples, used without further purification: 15C5 (Merck), 18C6 (Merck), DT18C6 (Parish) and (222) (Merck).

The salts $Mg(ClO_4)_2$ (Johnson Matthey), $Ca(ClO_4)_2 \cdot 6H_2O$ (Johnson Matthey), $Sr(ClO_4)_2 \cdot H_2O$ (Johnson Matthey) and $Ba(ClO_4)_2$ (Merck) were used for the calorimetric and potentiometric titrations. Solutions of the non-anhydrous Ca^{2+} and Sr^{2+} salts were dried over molecular sieves. For the conductometric titrations, the heptafluorobutyrates of the alkaline earth cations were prepared by adding the solid alkaline earth hydroxides to a concentrated aqueous solution of heptafluorobutyric acid (Aldrich) until no dissolution of the hydroxide could be observed. The solution was filtered and evaporated. The residue was washed with methylene chloride and dried in vacuo.

Propylene carbonate (PC, Merck p.a.) was used as the solvent. The water content was estimated by Karl–Fischer titration to be less than 0.1%.

For some non-cyclic ligands, the complex formation with alkaline earth cations was studied using conductometric titrations. To avoid dilution effects of the salt solution, a solution containing the ligands (2×10^{-2} M) and the salt (2×10^{-3} M) was titrated into a pure salt solution of an identical concentration. The treatment of the experimental data to calculate the stability constant has already been described in the literature [7, 8]. The reproducibility of the stability constants calculated from conductivity measurements are $\log K = \pm 0.03$.

Stability constants smaller than $10^5\,M^{-1}$ and all reaction enthalpies for the complexation reaction

$$M^{2+} + L \rightleftharpoons ML^{2+} \qquad K = \frac{[ML^{2+}]}{[M^{2+}][L]}$$

were determined using a Tronac Model 450 calorimeter. The determination of the stability constants and the reaction enthalpies from the measured thermograms is well known [9].

A solution of the ligand (0.06–0.08 M) was added to a solution of the salt ($(3\text{–}6) \times 10^{-3}$ M). After correction of all non-chemical contributions to the measured heat, the stability constant and the reaction enthalpy can be calculated from the thermogram. If the stability constant is higher than $10^5\,M^{-1}$, only the value of the reaction enthalpy is obtained. The experimental reproducibilities of the stability constants and reaction enthalpies are $\log K$, ±0.05; ΔH, ± 1 kJ mol^{-1}.

Some of the non-cyclic ligands did not form 1:1 complexes under the above-mentioned experimental conditions. To ensure the formation of 1:1 complexes in the reaction vessel of the calorimeter, the ligand concentration was reduced (0.03–0.04 M) and the salt concentration increased (0.02–0.05 M). The calorimetric titration was only performed for a short period. Thus, the salt concentration in the reaction vessel of the calorimeter was much higher compared with the ligand concentration. These titrations allow only the calculation of ΔH values from the thermograms.

The stability constant of the Ba^{2+} complex with 18-crown-6 was obtained from a competitive calorimetric titration [10] with the macrocyclic ligand diketopyridino-18-crown-6. A solution of the ligand 18C6 (0.08 M) was titrated into a solution containing diketopyridino-18C6 (0.026 M) and $Ba(ClO_4)_2$ (2.65×10^{-3} M). The experimental data for this reaction are: $\log K = 2.13$ and $-\Delta H = 27.7$ kJ mol^{-1}. Combining with the data for the reaction of diketopyridino-18C6 with Ba^{2+} in propylene carbonate ($\log K = 9.43$, $-\Delta H = 40.0$ kJ mol^{-1}), yields the stability of the complex formed with the ligand 18C6: $\log K = 11.56$. The realibility of the indirectly obtained stability constant for the reaction of 18C6 with Ba^{2+} can be demonstrated by comparing the values of the directly measured reaction enthalpy ($-\Delta H = 64.3$ kJ mol^{-1}) with the indirectly calculated enthalpy ($-\Delta H = 67.7$ kJ mol^{-1}).

The stability constants of the complexes with the cryptand (222) were measured using disproportionate potentiometric titrations with Ag^+ [11]. However, the dissociation of the Ba^{2+} complex was extremely slow. In the case of the Sr^{2+} complex, the dissociation reaction was complete after at least 18 days. During all potentiometric titrations, the ionic strength was kept constant at $I = 5 \times 10^{-2}$ M using tetraethylammonium perchlorate

(Fluka) as supporting electrolyte. The stability constants measured in this way are reproducible with an accuracy of $\log K = \pm 0.05$.

RESULTS AND DISCUSSION

The stability constants and the thermodynamic parameters for the complexation of alkaline earth cations by non-cyclic ligands are summarized in Table 1 and for the reaction with macrocyclic and macrobicyclic ligands in Table 2.

The stability constants given in Table 1 show that an increasing number of oxygen donor atoms in the ligand does not automatically result in higher values of the stability constants. Enthalpic and entropic contributions to the reaction often cancel each other. This is not surprising because the number of donor atoms increases with increasing chain length of the polyether and, in contrast, the steric requirements increase during the complex formation with a cation due to the fact that the ends of the ligands meet each other.

TABLE 1

Stability constants, $\log K$ (K in M^{-1}), and thermodynamic parameters, ΔH and $T\Delta S$ ($kJ\,mol^{-1}$), for the reaction of polyethylene glycoldimethylethers with alkaline earth cations in propylene carbonate at 25°C

Ligand	Parameter	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
DG	$\log K$	–	–	–	–
	$-\Delta H$	3.6	19.1	13.0	17.2
	$T\Delta S$				
TG	$\log K$	–	–	–	–
	$-\Delta H$	6.9	29.9	27.3	32.6
	$T\Delta S$				
TeG	$\log K$	2.06 [a]	2.43 [a]	3.69 [a]	4.30 [a]
	$-\Delta H$	15.6	30.6	38.8	39.4
	$T\Delta S$	−3.9	−16.8	−17.8	−15.0
PG	$\log K$	2.47 [a] 2.57 [b]	4.07 [a]	5.21 [a]	>5.5
	$-\Delta H$	17.2	38.0	49.1	51.5
	$T\Delta S$	−3.2	−14.9	−19.5	
HG	$\log K$	2.11 [a]	4.24 [a]	4.68 [a]	5.01 [a]
	$-\Delta H$	22.8	44.0	56.4	56.6
	$T\Delta S$	−10.8	−19.9	−29.8	−28.1

[a] Determined by conductometric titrations.

[b] Determined by calorimetric titrations.

TABLE 2

Stability constants, log *K* (K in M^{-1}), and thermodynamic parameters, ΔH and $T\Delta S$ (in kJ mol^{-1}), for the reaction of crown ethers and cryptands with alkaline earth cations in propylene carbonate at 25°C

Ligand	Parameter	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
15C5	log *K*	3.46 [a]	>5 [a,b]	>5 [a,b]	>5 [a,b]
	$-\Delta H$	27.5	33.9	41.6	39.2
	$T\Delta S$	−7.8			
18C6	log *K*	2.94 [a]	3.68 [a]	>5 [a]	11.56 [c]
	$-\Delta H$	30.2	38.5	59.1	64.3
	$T\Delta S$	−13.5	−17.6		1.4
DT18C6	log *K*	<1 [a]	2.70 [a]	2.19 [a]	3.07 [a]
	$-\Delta H$	3.2	7.7	17.0	22.3
	$T\Delta S$		7.6	−4.6	−4.9
(222)	log *K*	10.73 [b]	10.76 [d]	12.89 [b]	17.1 [e]
	$-\Delta H$	39.0	63.8	76.2	105.1
	$T\Delta S$	22.0	−2.7	−3.0	−7.9

[a] Determined by calorimetric titrations. [b] Determined by potentiometric titrations. [c] Determined by calorimetric competition titrations. [d] From ref. 13. [e] From ref. 14.

The measured values of the reaction enthalpies for the complexation of cations by non-cyclic polyethers depend on the number of oxygen donor atoms of the ligands. However, this is not a perfect correlation, as can be seen as an example for Mg^{2+} and Ba^{2+} in Fig. 1. In the case of the complexation of Sr^{2+} with the smallest non-cyclic ligand DG and for the reaction of Ba^{2+} with the largest non-cyclic ligand HG, the measured values of the reaction enthalpies are smaller than expected from comparison with the values measured for the other ligands. For the other cations examined, there is a linear correlation between the measured values of the reaction enthalpies and the number of oxygen donor atoms of the non-cyclic ligands, A mean interaction energy between one cation and one donor atom of the acyclic polyethers can be calculated from the slopes; these values are given in Table 3.

The results given in Table 2 clearly show that the macrocyclic polyethers 15C5 and 18C6 form more stable complexes than the non-cyclic polyethers. If the cavity dimensions and ionic dimensions are similar, the strongest complexes are formed.

The replacement of two oxygen donor atoms by two sulphur donor atoms results in a decrease in the stabilitiers of the complexes formed compared with the ligand 18C6. This is mainly caused by a drastic reduction in the values of the reaction enthalpies.

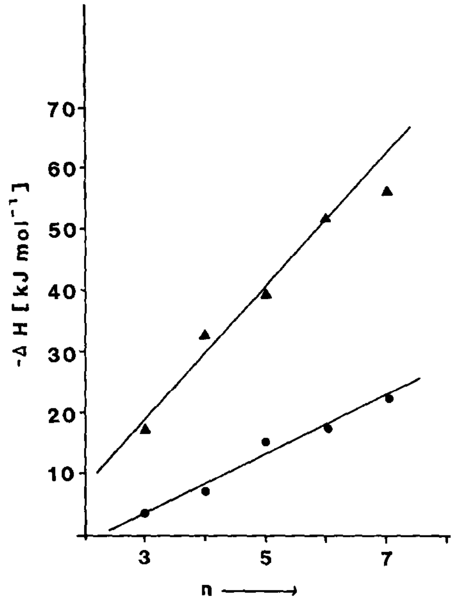

Fig. 1. The experimentally measured reaction enthalpies ΔH as a function of the number of ether donor atoms *n* of non-cyclic polyethers for the complexation of Mg^{2+} (●) and Ba^{2+} (▲) in propylene carbonate.

The macrocyclic cryptand (222) forms the most stable complexes of all ligands examined. For the cations Ca^{2+}, Sr^{2+} and Ba^{2+}, enthalpic contributions only are responsible for these results; for Mg^{2+}, enthalpic and entropic contributions are responsible.

The experimental results obtained in propylene carbonate for the complexation behaviour of non-cyclic, macrocyclic and macrobicyclic ligands are comparable with the results obtained in other solvents [5, 12].

To decide the origin of the macrocyclic effect for the cations examined and unsubstituted crown ethers, one may use the values of the mean interaction energies between one oxygen donor atom and the cations given in Table 3 to calculate values of the reaction enthalpies of crown ethers with these cations. These results are summarized in Table 4. If the cations are too big to fit into the cavity of the ligand, the calculated values

TABLE 3

Mean interaction energies ΔH_i (kJ mol^{-1}) between one cation and one oxygen donor atom of the non-cyclic ligands in propylene carbonate

	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
$-\Delta H_i$	4.9 ± 0.5	5.9 ± 0.4	9.8 ± 0.4 [a]	11.0 ± 0.5 [b]

[a] Calculated without the value of DG. [b] Calculated without the value of HG.

TABLE 4

Experimental values of the reaction enthalpies ΔH_{exp} (kJ mol^{-1}) for the complexation of alkaline earth cations by the crown ethers 15C5 and 18C6, together with the calculated values of the reaction enthalpies ΔH_{cal} (kJ mol^{-1}) using the values given in Table 3

Ligand	Parameter	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
15C5	$-\Delta H_{exp}$	27.5	33.9	41.6	39.2
	$-\Delta H_{cal}$	24.5	29.5	49.0	55.0
18C6	$-\Delta H_{exp}$	30.2	38.5	59.1	64.3
	$-\Delta H_{cal}$	29.4	35.4	58.8	66.0

of the reaction enthalpies are higher than the experimental ones, because not all the donor atoms of the ligand are able to achieve optimal interaction with the complexed cations. For the ligand 18C6, the calculated and experimental reaction enthalpies are identical with experimental error for all cations. It can be assumed that this ligand wraps around the cations which are too small compared with the dimensions of the cavity. The higher stability constants of crown ether complexes compared with the complexes of the acyclic polyethers can only result from entropic factors. Similar results have been reported in methanol as solvent [5]. The non-cyclic ligands have to adopt a cyclic structure during complex formation which is already partly pre-organized in the crown ether molecules.

No conclusions concerning the origin of the macrobicyclic effect are possible at present, because no energies of interaction of nitrogen donor atoms with alkaline earth cations have been reported so far.

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