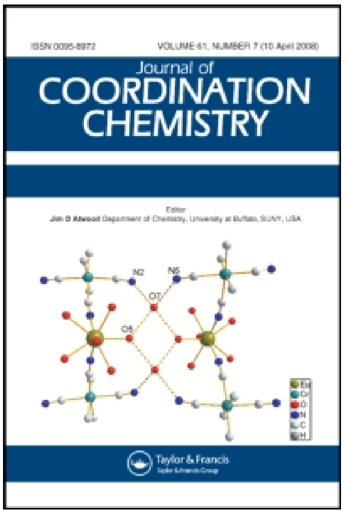

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COMPLEXATION OF ALKALINE EARTH CATIONS BY NONCYCLIC POLYETHERS, CROWN ETHERS, AND CRYPTANDS IN ACETONE

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The complexation of akaline earth cations by non-cyclic polyethers, crown ethers and cryptands was studied in acetone by means of potentiometric and calorimetric titrations. The results show that the stabilities of the complexes decrease in the order: cryptands, crown ethers and noncyclic polyethers. Interactions between the different ligands and solvent molecules influence the stability of the complexes formed when compared with methanol as solvent.

KEYWORDS: Polyethers, crown ethers, cryptands, complexes, thermodynamics, acetone

INTRODUCTION

The formation of complexes of crown ethers and cryptands with alkaline earth cations has been studied using different experimental methods.[1] However, up to now the most commonly used solvent is methanol. Data in other solvents are rare. For the understanding of all factors influencing measured stability constants it is necessary to have more experimental data in other solvents than those already reported.

The stability of complexes formed in solution also depends on the chemical structure of the ligands. Macrobicyclic ligands in most cases form stronger complexes as compared with macrocyclic ligands.[1] On the other hand, these complexes are more stable than those of noncyclic ligands.[2,3] To obtain more information about the origin of the so-called macrocyclic and macrobicyclic effects, the complexation behaviour of different types of ligands in acetone has been studied.

EXPERIMENTAL

Materials

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

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(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 the commercial samples of the ligands was not sufficient they were distilled under reduced pressure prior to use.

The macrocyclic and macrobicyclic ligands used were commercial samples and used without further purification (Fig. 1). $Ca(ClO_4)_2 \cdot 4\,H_2O$ (Johnson Matthey Chemicals), $Sr(ClO_4)_2 \cdot 6\ H_2O$ (Johnson Matthey Chemicals), $Ba(ClO_4)_2$ (anhydrous; Merck) and $AgBF_4$ (Merck) were of the highest purity commercially available. Tetraethylammonium perchlorate (TEAP, Fluka) acted as supporting electrolyte during potentiometric titrations. Acetone (Fluka; H_2O content less than 0.4%) was used as solvent.

Methods

A Tronac calorimeter (Model 450) was used to measure all reaction enthalpies and stability constants smaller than log K = 5. During a calorimetric titration a solution of the ligand (0.06 - 0.08 mol dm^{-3}) was titrated into a solution of the salt (4 - 6 × 10^{-3} mol dm^{-3}). The measured heat, Q, after correction for all non-chemical effects, depends on the reaction enthalpy, ΔH, and the number of moles, Δn, of the complex formed as shown below.

$$Q = \Delta H \cdot \Delta n$$

The theory of calorimetric titrations has already been described in detail in the literature.[4-6] If stability constants are higher than $K = 10^5\ dm^3\ mol^{-1}$, the number of moles of the complex formed during the titration is constant and equal to the number of moles of ligand added. In this case only values of the reaction enthalpy can be calculated.

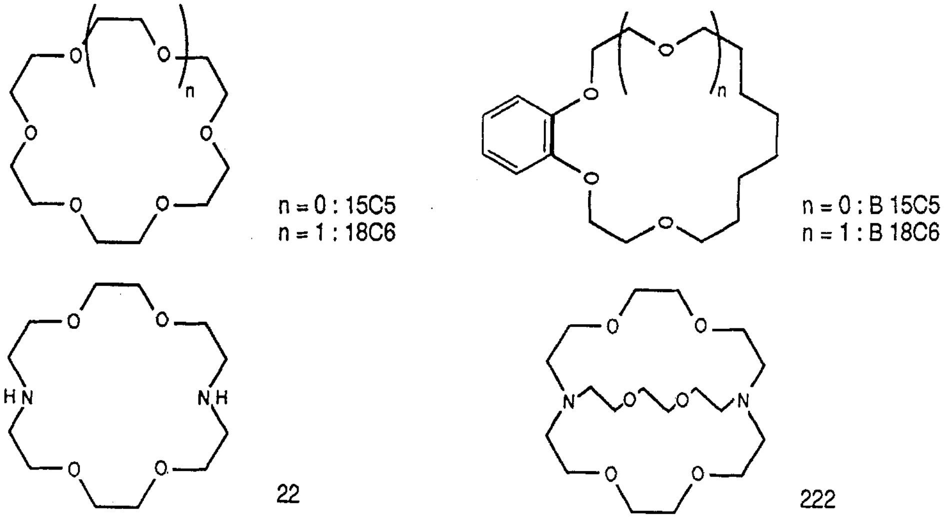

Figure 1 Chemical structures of the macrocyclic and macrobicyclic ligands used in this work.

Competitive calorimetric reactions can be used to obtain stability constants, which are too high for a direct measurement, indirectly. During such titrations a ligand solution (0.08 mol dm^{-3}) was added to a solution containing a salt (5×10^{-3} mol dm^{-3}) and another ligand (0.03 mol dm^{-3}).[7] The accuracy of this method can be seen by comparison of the directly and indirectly measured values of the reaction enthalpies (see Table 2).

The following competitive calorimetric reactions were performed:

a) 18C6 + (Sr^{2+} + HG) : log K = 2.79, ΔH = −15.3 kJ mol^{-1},
b) 18C6 + (Ba^{2+} + HG) : log K = 3.07, ΔH = −18.9 kJ mol^{-1},
c) B18C6 + (Ba^{2+} + HG) : log K = 1.52, ΔH = −10.5 kJ mol^{-1},
d) 18C6 + (Ca^{2+} + B15K5) : log K = 1.03, ΔH = −18.1 kJ mol^{-1},
e) B18C6 + (Ca^{2+} + B15C5) : log K = 2.01, ΔH = −15.8 kJ mol^{-1}.

No ion-selective electrodes which can be used in organic solvents are known for the alkaline earth cations. However, competitive reactions with Ag^+ are possible since the concentration of this ion can easily be measured.[8,9] During the titrations the ionic strength was kept constant at I = 0.05 mol dm^{-3} using TEAP. Only the stability constant of the complex of the cryptand (222) with ca^{2+} was determined by a competitive potentiometric reaction with Ag^+. After mixing the corresponding solutions it takes nearly eight hours until equilibrium is reached. Assuming that this reaction should be slower in cases of complexes with Sr^{2+} and Ba^{2+} (as observed in other solvents), no further competitive reactions were performed.[10] The ligand (22) forms precipitates with $Sr(ClO_4)_2$ and $Ba(ClO_4)_2$ in the presence of TEAP. Under these circumstances no potentiometric titrations could be performed. The accuracy of the experimental techniques used to study complex formation of alkaline earth cations with the different ligands has already been tested.[9,11]

RESULTS AND DISCUSSION

Values of stability constants and thermodynamic parameters for the complexation of alkaline earth cations by noncyclic polyethers are given in Table 1, and for complexes with crown ethers and the cryptand (222) in Table 2. Incomplete dissociation of alkaline earth salts is possible in acetone. However, it is known that the formation of ion-pairs can be neglected at the concentrations used in the case of the alkaline earth perchlorates.[12,13] Even a considerable concentration of ion-pairs in solution does not affect the "apparent" complexation constant if the ion-pairing constants differ by more than one order of magnitude.[13]

Experimentally measured stability constants and reaction enthalpies reflect the influence of different factors. Complexation of the biggest cation, which is solvated weakly, results in the most stable complexes of all cations examined. The number of donor atoms in the ligands also is important for complex stability. If the ligand is too small compared to the size of the cation, only a part of the cation solvating molecules are replaced by the ligand. On the other hand, not all donor atoms of the ligand may interact with the cation if the ligand is too large for the cation. In this case the ends of the ligands wrapped around the cation may experience repulsive interactions.

All cations examined form more stable complexes with crown ethers when compared with the non-cyclic polyethers. Even cations too big to fit into the ligand

Table 1 Stability constants (K in dm^3 mol^{-1}) and thermodynamic parameters (ΔH and TΔS in kJ mol^{-1}) for the complexation of alkaline earth cations by polyethylene glycol dimethylethers in acetone at 25°C, determined by calorimetric titrations.

Ligand	Value	Ca^{2+}	Sr^{2+}	Ba^{2+}
DG	log K			
	-ΔH			2.0
	TΔS			
TG	log K			
	-ΔH	6.1	8.1	16.4
	TΔS			
TeG	log K	2.49	2.56	3.27
	-ΔH	26.8	36.9	27.8
	TΔS	-12.7	-22.4	-9.2
PG	Log K	2.51	2.49	3.97
	-ΔH	39.8	42.6	39.9
	TΔS	-25.5	-28.5	-17.3
HG	log K	2.43	2.52	4.28
	-ΔH	44.7	40.9	40.1
	TΔS	-30.9	-26.6	-15.8

cavities show strong complexation. Comparison of the reaction enthalpies of non-cyclic and macrocyclic ligands indicates that for the crown ether 15-crown-5 high values of stability constants are caused by entropic factors. With increasing ring size, enthalpies favour complex formation due to an increase of the number of ligand donor atoms and improved interaction between those and the cations.

Benzo groups in the ligands are responsible for a reduction of reaction enthalpies. Ether donor atoms located on an aromatic ring system show a different basicity as compared with other ether donor atoms. Thus, a reduction of reaction enthalpy is observed if the cation interacts with all donor atoms of the ligand. If the complexed cation is too small for the cavity of the macrocyclic ligand the benzo groups do not influence the reaction enthalpy. This observation may result from the fact that not all donor atoms of these ligands can interact with the complexed cation.

The substitution of two ether donor atoms by nitrogen causes a considerable reduction in the observed stability constants, mainly caused by enthalpic contributions. Ether donor atoms obviously interact stronger with alkaline earth cations than nitrogen. On the other hand, interactions of the diaza crown ether with solvent molecules are obviously more important in methanol than in acetone. As a result, weaker complexes in methanol are observed.[14] This has to be attributed to lower values of reaction enthalpies for complex formation between alkaline earth cations and the ligand (22) in methanol as compared with acetone as solvent. Reaction enthalpies differ by some 30 kJ mol^{-1}. The strong solvation of the ligand (22) in methanol is also underlined by the high positive values of reaction entropies. In acetone, they are close to zero as far as could be determined.

The macrobicyclic ligand (222) forms the most stable complexes of all ligands examined. This can be attributed to high values of reaction enthalpies with this ligand. Compared to results obtained in methanol, the reaction enthalpies in acetone are much higher for the complexation of alkaline earth cations.[14] Even if

Table 2 Stability constants (K in dm^3 mol^{-1}) and thermodynamic parameters (ΔH and TΔS in kJ mol^{-1}) for the complexation of alkaline earth cations by crown ethers and cryptands in acetone at 25°C, determined by calorimetric titrations (values of ionic and cavity radii are taken from the literature[16,17]).

Ligand	Value	Ca^{2+} (r = 1.00 Å)	Sr^{2+} (r = 1.16 Å)	B^{2+} (r = 1.36
15C5	log K	4.01	[a]	[a]
(r = 0.9 Å)	-ΔH	35.2	31.3	31.9
	TΔS	-12.4		
B15C5	log K	4.04	[a]	[a]
	-ΔH	26.3	24.8	18.9
	TΔS	-3.4		
18C6	log K	5.07[b]	5.31[b]	7.35[b]
(r = 1.4 Å)				8.54[c]
	-ΔH	38.9	52.0	61.0
		44.4[b]	56.2[b]	59.0[b]
	TΔS	-10.1	-21.8	-19.2
B18C6	log K	6.05[b]	4.39	5.80[b]
	-ΔH	40.7	46.1	49.3
		42.1[b]		50.6[b]
	TΔS	-14.2		-16.4
(22)	log K	4.61	>5	>5
	-ΔH	29.8	36.5	41.4
	TΔS	-3.6		
(222)	log K	12.9[d]	>5	>5
(r = 1.4 Å)	-ΔH	73.5	73.7	91.7
	TΔS	-0.2		

[a] 1:1 and 2:1 Complex formation. [b] Calorimetric competitive titration. [c] Ref. 15. [d] Potentiometric titration.

no values are known for cation solvation in acetone, interactions mainly between the cryptand and solvent molecules may be responsible.

Stability constants of all complexes of the alkaline earth cations with non-cyclic polyethers are several orders of magnitude smaller as compared with macrocyclic polyethers. However, in some cases the reaction enthalpies in the case of the non-cyclic ligands are higher than those of macrocyclic ligands. Higher stability constants of the crown ethers are therefore caused by favourable entropic contributions. During complex formation, the non-cyclic ligand has to wrap around the cations. This reaction is accompanied by a decrease in the entropy of the complete system. The crown ethers and the cryptand already possess a more or less pre-organized cavity. Thus, during complex formation, other influences processes, *e.g.*, the desolvation of the ligand and cation, become predominant. As a result, the reaction entropy may increase due to the release of solvent molecules.

The results clearly demonstrate the influence of the solvent upon the strength of the complexes formed. However, beside solvation of the cations, interactions of the ligands with solvent molecules have to be taken into account as well.

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