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INFLUENCE OF DIFFERENT DONOR ATOMS ON THE FORMATION OF 1:1- AND 2:1-COMPLEXES OF 12-CROWN-4 AND 18-CROWN-6 ETHERS WITH Ag^+, Tl^{2+}, Ba^{2+} AND Pb^{2+}

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ABSTRACT

Log K, ΔH, and $T\Delta S$ values for the interaction of 18-crown-6, diaza-18-crown-6 and dithia-18-crown-6 with Ag^+, Tl^{2+}, Ba^{2+}, and Pb^{2+} have been measured in methanol solutions. A detailed discussion of the influence of different donor atoms upon complex formation may be made. Enthalpic and entropic contributions can be discussed separately. The situation is more difficult to discuss in the case of the reactions of the different 12-crown-4 ethers. However, the varying donor atoms play an important role in the formation of 1:1- and 2:1-complexes.

INTRODUCTION

Soon after the discovery of the complexation abilities of crown ethers towards alkali and alkaline earth cations [1], the influence on the complex formation caused by substituting one or two oxygen donor atoms of 18-crown-6 (18C6) by nitrogen or sulphur atoms was studied [2]. It was found that the substitution of oxygen atoms lead to a decrease in stability of the K^+-complexes and to an increase in stability the Ag^+-complexes.

In the meantime more data about reactions between crown ethers with different donor atoms and some mono- and bivalent cations have been reported. A complete compilation of all thermodynamic results published up to early 1984 for the complexation of cations by mono- and bicyclic ligands has been done by Izatt et al. [3]. A detailed explanation of the rather different behaviour of the substituted crown ethers is not available [4]. In order to obtain more information about this we decided to study the complex formation between substituted crown ethers and some cations in methanol solutions. The cations chosen for this study, Ag^+, Tl^+, Ba^{2+}, and Pb^{2+}, are of different types. Using the classification of Pearson [5,6], the barium ion is a hard cation and the thallium ion is a soft cation, mainly bonded by means of cation-dipole interactions. For soft cations, such as Ag^+ and Pb^{2+}, covalent contributions to the binding energies become more important.

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The influence of all factors mentioned above in the formation of 2 : 1-complexes (ratio of ligand to cation) has so far not been measured. Therefore, The complexation behaviour of different substituted 12-crown-4 ethers was also investigated.

EXPERIMENTAL

Materials

The salts used, $AgNO_3$ (Merck), TlAc (Ventron), $Ba(ClO_4)_2$ (Merck) and $Pb(NO_3)_2$ (Merck), are anhydrous and of the highest purity.

The following ligands (see Fig. 1) were commercial samples and used without further purification: 12C4 (Merck), (11) (Merck) 18C6 (Merck), (22) (Merck), and DT18C6 (Parish). The ligand DT12C4 was synthesized and purified according to published procedures [7].

Procedure

Stability constants smaller than $10^{5.5}$ and reaction enthalpies were determined using a Tronac Model 450 calorimeter [8–10]. The formation of 1 : 1-complexes can be described by eqn. (1):

$$M^{n+} + L \rightleftharpoons ML^{n+} \qquad (1)$$

with

$$K_1 = \frac{[ML^{n+}]}{[M^{n+}][L]}$$

The stability constants higher than $10^{5.5}$, and stability constants for the formation of 1 : 1- and 2 : 1-complexes, were measured by means of ion selective electrodes for the reaction of Ag^+ (Metrohm EA 282) and Pb^{2+} (Metrohm EA-306Pb). This experimental technique has already been de-

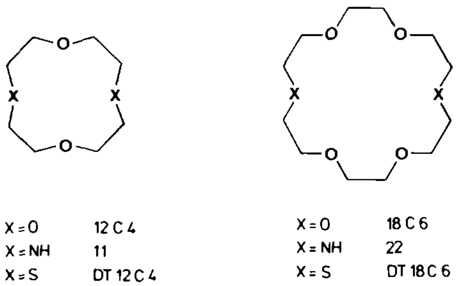

Fig. 1. Macrocyclic ligands used in this work.

scribed [11]. In all remaining cases, competitive potentiometric [12,13] or competitive calorimetric titrations [14] were performed to estimate the stability constants or the reaction enthalpies.

The sum of the reaction enthalpies ΔH_{ov} for the formation of 1 : 1- and 2 : 1-complexes was measured in the following way. A solution of the cryptand (222) (0.03–0.08 N) was titrated into a solution containing a salt ($6-8 \times 10^{-4}$ N) and a high excess of the ligand ($2-3 \times 10^{-2}$ N). Under these experimental conditions the formation of 2 : 1-complexes is complete. Using the separate estimated value for the reaction enthalpy of the cryptand (222) with Ag^+ ($\Delta H_{cry} = -68.3$ kJ mol^{-1} [15]), Tl^+ ($\Delta H_{cry} = -81.7$ kJ mol^{-1}), Ba^{2+} ($\Delta H_{cry} = -68.2$ kJ mol^{-1}) and Pb^{2+} ($\Delta H_{cry} = -72.7$ kJ mol^{-1} [16]), ΔH_{ov} can be calculated from the observed reaction enthalpy ΔH_{obs}: $\Delta H_{ov} = \Delta H_{cry} - \Delta H_{obs}$. The value of the reaction enthalpy ΔH_1 for the formation of 1 : 1-complexes can be measured independently. Thus, the value of the reaction enthalpy ΔH_2 for the formation of the 2 : 1-complex, according to reaction (2), can be calculated from ΔH_{ov}.

$$ML^{n+} + L \rightleftharpoons ML_2^{n+} \qquad (2)$$

with

$$K_2 = \frac{[ML_2^{n+}]}{[ML^{n+}][L]}$$

This experimental method gave no definite result for the formation of a 2 : 1-complex of Ba^{2+} with the ligand (11). A positive value of the reaction

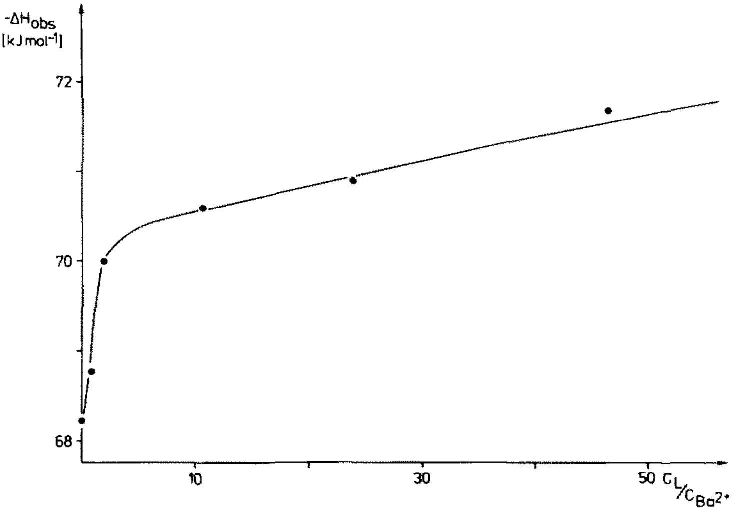

Fig. 2. Observed reaction enthalpies ΔH_{obs} for the titrations of solutions containing K^+ and (11) at different ratios of ligand to cation concentration with the cryptand (222), in methanol at 25 °C.

enthalpy ΔH_{ov} was observed (see Fig. 2). Even at a ligand concentration forty times higher than the Ba^{2+} concentration, no limiting value was observed.

RESULTS AND DISCUSSION

Log K, ΔH, and $T\Delta S$ values for the reactions of 18-crown-6 ethers and 12-crown-4 ethers, with different donor atoms, with Ag^+, Tl^+, Ba^{2+}, and

TABLE 1

Log K (K in M^{-1}), ΔH (kJ mol^{-1}), and $T\Delta S$ (kJ mol^{-1}) for the reaction of several cations with crown ether ligands containing different donor atoms, in methanol at 25°C

Ligand	Parameter	Ag^+	Tl^{2+}	Ba^{2+}	Pb^{2+}
		(r = 1.15 Å) [a]	(r = 1.50 Å) [a]	(r = 1.36 Å) [a]	(r = 1.18 Å) [a]
18C6	log K	4.58 [c]	5.22	7.31 [d]	6.99
(r = 1.4 Å) [b]	$-\Delta H$	39.1	50.9	48.5	45.0
	$T\Delta S$	−13.1	−21.2	−7.0	−5.3
(22)	log K	10.02 [e]	3.06	6.12 [f]	9.11 [g]
	$-\Delta H$	44.9	21.2	10.0	29.1
	$T\Delta S$	12.0	−12.8	24.8	22.7
DT 18C6	log K	10.33 [h]	3.93	–	4.76
	$-\Delta H$	64.0	11.2		34.5
	$T\Delta S$	−5.3	11.1		−7.5
12C4	log K_1	1.61 [i]	3.22	2.56 [i]	1.77
(r = 0.6 Å) [b]	$-\Delta H_1$	10.7	9.4	21.4	13.9
	$T\Delta S_1$	−1.6	8.9	−6.9	−3.8
	log K_2	1.90	$\leqslant 3$	< 2	2.11
	$-\Delta H_2$	27.9	10.6	5.6	9.6
	$T\Delta S_2$	−17.1			2.4
(11)	log K_1	6.514	2.48	2.34	7.22
	$-\Delta H_1$	31.9	28.5	13.3	27.2
	$T\Delta S_1$	5.1	−14.4	−4.4	13.8
	log K_2	3.01	$\leqslant 3$	< 2	1.73
	$-\Delta H_2$	21.5	−8.0	> -15	−4.7
	$T\Delta S_2$	−4.4			14.5
DT12C4	log K_1	7.56	3.87	–	4.01
	$-\Delta H_1$	60.8	2.9	–	2.4
	$T\Delta S$	−17.8	19.1	–	20.4
	log K_2	5.29	$\leqslant 3$	–	1.78
	$-\Delta H_2$	≈ 0	7.7	–	5.0
	$T\Delta S_2$	≈ 30	–	–	5.1

[a] from ref. 21. [b] from ref. 20. [c] from ref. 11. [d] from ref. 14. [e] from ref. 22. [f] from ref. 23. [g] from ref. 24. [h] from ref. 25. [i] from ref. 26.

TABLE 2

Experimental estimated medium bond energies (kJ mol^{-1}) in methanol

	Ag^+	Pb^{2+}
O	6 [a]	3–8 [b]
NH	22 [a]	14 [b]
S	25 [c]	<1 [c]

[a] from ref. 15. [b] from ref. 16. [c] from ref. 27.

Pb^{2+} are summarized in Table 1. The measured stability constants for the complexation of Tl^+ by the ligands 18C6 [17] and (22) [18] agree very well with published values. The same is true for the reaction enthalpy obtained for the reaction of 18C6 with Pb^{2+} [19]. No data for the reactions of 12C4, (11), and DT12C4 are available for comparison.

Effect of different atoms on 18-crown-6 ethers

The diameter of 18C6 ($r = 1.4$ Å [20]) is only slightly too small for the Tl^+ ion (see Table 1) to accommodate it without any deformations. The measured reaction enthalpies for Tl^+ and Ba^{2+} decrease in the following manner if two oxygen donor atoms are substituted by other donor atoms: O > NH > S. This is not surprising because cation–dipole interactions are mainly responsible for the interactions between ligands and these cations. The electronegativity of the heteroatoms decreases in the same way.

In the case of the complex formation with Ag^+ and Pb^{2+}, the situation becomes much more difficult to explain due to the covalent contributions to the binding energies. Thus, it is necessary to know the individual bond strength between both cations and the different ligand donor atoms. The experimentally estimated bond energies are summarized in Table 2. For the ligand (22), the measured values of the reaction enthalpies are lowered due to conformational changes of the ligand during the complex formation [15,21] (see Fig. 3). Such a phenomenon has not been reported for DT18C6. With this information, the observed reaction enthalpies for the complexation of Ag^+ and Pb^{2+} can be explained without difficulty. In case of the Ag^+ ion,

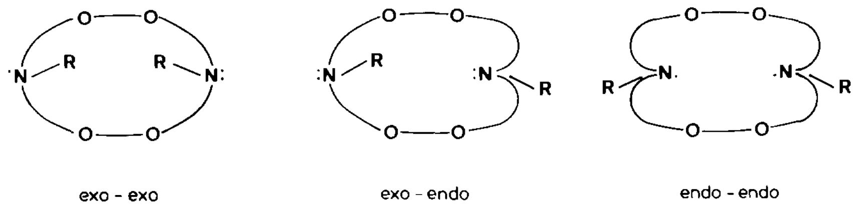

Fig. 3. Conformational forms of the uncomplexed ligand (22).

one expects the following sequence for the decrease in the measured values of the reaction enthalpies due to different donor atoms: S > NH > O; for Pb^{2+} the sequence is O > S > NH.

The experimental results are identical with this prediction. However, values for the reaction entropies show quite a different trend. For all cations, with the exception of Tl^{+}, one gets:

$NH > S \geqslant O$

This order seems to be independent of the cation complexed. Therefore, these results can be attributed to interactions between the ligand and solvent molecules. The aza crown ether (22) exists in different conformational forms (see Fig. 2). In a polar medium like methanol, the lone electron pairs of the nitrogen atoms are mainly direct outside the cavity. Under these circumstances interactions between the ligand and methanol molecules are possible, leading to an ordered structure in the solvent near the nitrogen atoms. These solvent molecules are liberated during complex formation with a cation because the ligand has to adopt the endo–endo conformation. Thus, the reactions of the ligand (22) are favoured by entropic contributions. The interactions between the other donor atoms and the solvent are much weaker.

It is possible to test the considerations made above. Substitution of the protons of the amino groups of (22) by long alkyl chains should lead to a preference for the endo–endo conformation of the uncomplexed ligand, for sterical reasons. The observed reaction entropies should be very similar to those found in the reactions of 18C6 and DT18C6. All known experimental results support the explanation given above [22–24].

The deviation behaviour of the Tl^{+} ion can easily be attributed to its size. The ion is too big to be complexed without any structural deformation of the different ligands. However, the cavity diameter of DT18C6 is slighty bigger than that of 18C6; with the increasing radii of the different donor atoms in comparison with oxygen, the ligand cavities are enlarged. The sterical requirements during the complex formation with Tl^{+} are, therefore, the lowest for the ligand DT 18C6.

Generally, the complexation reactions of bivalent cations, compared with monovalent cations, are favoured by reaction entropies. The bivalent cations are solvated stronger than the monovalent ones and therefore more solvent molecules are liberated during complex formation. However, the ligand simultaneously loses structural flexibility. The accumulation of all the different effects finally gives the measured reaction entropies.

Effect of different donor atoms on 12-crown-4 ethers

The diameter of these ligands ($r = 0.6$ Å) [20] are much too small to completely surround one of the cations used in this study. Therefore, the formation of 2 : 1-complexes is possible. The measured reaction enthalpies for the 1 : 1-complex formation do follow the trends already discussed. A few exceptions may occur because, for sterical reasons, not all donor atoms of the small ligands may interact equally with the complexed cations. The same is true for the observed reaction entropies.

A detailed discussion of the 2 : 1-complex formation is not possible due to the very complex situation. The values of the reaction enthalpies, ΔH_2, for the binding of the second ligand molecule are equal to, or even smaller than, the values for the reaction of the first ligand. For the second complexation step of the ligand (11) with Tl^+, Ba^{2+}, and Pb^{2+}, even positive values of ΔH_2 are measured; conformation changes during the reactions (see Fig. 2) are responsible for this. However, the second ligand molecule liberates more than one solvent molecule attached to the cation. The formation of the 2 : 1-complexes are favoured by entropic contributions.

Different behaviour is observed in the reaction between 12C4 and Ag^+. The value of ΔH_2 is more than double that of ΔH_1. The formation of the 2 : 1-complex is disfavoured by the reaction entropies. These experimental findings can be explained in the following way. During the formation of the 1 : 1-complex, the interactions of the unsubstituted solvent molecules next to the cation are disturbed. Therefore, less energy is necessary for the replacement of further solvent molecules by the second ligand molecule, and also less entropy is gained. Similar observations in the reactions of other crown ethers which are able to form 2 : 1-complexes have been reported [11].

CONCLUSIONS

The types of donor atoms of 18-crown-6 and 12-crown-4 ethers are rather important in the formation of complexes with different kinds of cations. It is possible to control the selectivity of a ligand against a certain cation by means of the donor atoms of the ligand. For each type of cation (hard or soft), an optimal crown ether is always available or may be synthesized if one knows the strength of interaction between the specific cation and all possible donor atoms. However, structural changes of the ligand during complexation must also be taken into account.

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