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cis-Benzenetrioxid, 9-Crown-3 and 12-Crown-4 as Ligands for the Complexation of Cations in Different Solvents

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Abstract

The reaction of *cis*-benzenetrioxid with mono- and bivalent cations was measured by means of calorimetric titrations in methanol solutions. From these measurements we can only conclude a distinct reaction between this ligand and Ba^{2+}. By means of NMR spectroscopy stability constants for Ca^{2+}, Sr^{2+}, and Ba^{2+} were obtained. Only the formation of the Ba^{2+} complex produces enough heat for studying this reaction by calorimetric titrations in other solvents. Therefore, the reactions between the Ba^{2+} cation and *cis*-benzenetrioxid, 9-crown-3, and 12-crown-4 were studied. From the reaction enthalpies measured for the formation of 1:1 and X:1 complexes (ratio of ligand to cation) conclusions about the complex stoichiometry can be drawn.

Introduction

Among the macrocylic ligands containing oxygen, *cis*-benzenetrioxid, see Fig. 1, holds an exceptional position. As seen in the drawing it looks quite simply like a real crown ether. However, for sterical reasons this ligand is not able to accommodate any ion. The distance between the oxygen donor atoms is too small [1]. Therefore, in crystalline complexes with *cis*-benzenetrioxid, different compositions between ligand and cation have been found. They depend upon the radii of the complexed cations [1–3].

Compared with *cis*-benzenetrioxid the ligand 9-crown-3 possesses an identical number of donor atoms. Up to now no data for the complexation of both ligands in solution have been reported. Thus, it is not known if the composition found in solid complexes with *cis*-benzenetrioxid exists also in solutions.

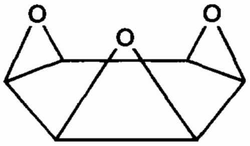

Fig. 1. *cis*-Benzenetrioxid.

Calorimetric titrations have been used to study the formation of complexes in solution [4]. Even in cases where complexes with a composition other than 1:1 are formed in solution, these methods give some information about the complex formation [5].

Experimental

Materials

All salts used were anhydrous and of the highest purity commercially available. Solutions containing Ba^{2+} in different solvents were prepared using anhydrous $Ba(ClO_4)_2$ (Merck). Under experimental conditions this salt is completely dissociated.

The synthesis of the ligands *cis*-benzenetrioxid (c-BTO) and 9-crown-3 (9C3) (Fig. 2) has been described already in the literature [6]. The crown ether 12-crown-4 (12C4; Merck) (Fig. 2) and the cryptand (222) (Merck) were used without further purification. As solvents methanol (Merck; H_2O content less than 0.01%), acetonitrile (Merck; H_2O content less than 0.3%), and propylene carbonate (Merck; p.a.) were chosen.

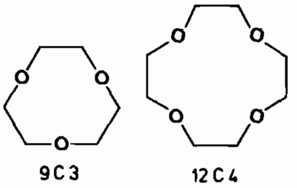

Fig. 2. 9-crown-3 (9C3) and 12-crown-4 (12C4).

Procedure

Stability constants and reaction enthalpies were determined using a Tronac Model 450 calorimeter. The formation of 1:1 complexes is given by eqn. (1):

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$$\mathrm{M}^{n+} + \mathrm{L} \rightleftharpoons \mathrm{ML}^{n+} \tag{1}$$

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

Special precautions have to be taken that only the formation of 1:1 complexes is observed since one expects all macrocylic ligands used to also form complexes with other compositions. To ensure the formation of the 1:1 complexes a solution of the ligands (0.06–0.07 N) is titrated continuously into a salt solution (0.02–0.03 N). Under these conditions the concentration of the salt inside the reaction vessel of the calorimeter is much higher during the titration compared with the ligand concentration. Due to the fact that the complex formation is complete at any time of the titration only the reaction enthalpy can be calculated using the thermogram. Afterwards, a second titration is performed to obtain the stability constant and reaction enthalpy for the 1:1 complex formation. Now a ligand solution (0.07 N) is titrated into a salt solution (5×10^{-3} N). After correction for all non-chemical heat effects the heat produced during the reaction is related to the reaction enthalpy by:

$$Q_t = \Delta n_{1,t} \Delta H_1$$

The number of moles of the 1:1 complex formed at the time t, $\Delta n_{1,t}$, is a function of the stability constant K_1. An iterative procedure is used to calculate the stability constant and reaction enthalpy from the thermogram [4].

The formation of the 2:1 complexes (ratio of ligand to cation) is described by eqn. (2):

$$\mathrm{M}^{n+} + \mathrm{L} \rightleftharpoons \mathrm{ML}^{n+} + \mathrm{L} \rightleftharpoons \mathrm{ML}^{n+}_2 \tag{2}$$

The first part of this reaction scheme is identical with eqn. (1). For the stability constant K_2 of the 2:1 complex one gets

$$K_2 = \frac{[\mathrm{ML}^{n+}_2]}{[\mathrm{ML}^{n+}][\mathrm{L}]}$$

To ensure the complete formation of 2:1 complexes a salt solution (0.01–0.02 N) is titrated into a ligand solution (7–9×10^{-3} N). During the titration the ligand concentration in the reaction vessel is much higher than the salt concentration. Thus, a complete formation of 2:1 complexes is probable. From the measured heat Q the sum of reaction enthalpies for the formation of 1:1 and 2:1 complexes is obtained:

$$Q = \Delta n(\Delta H_1 + \Delta H_2)$$

Without any information about the complexes formed in solution one generally gets:

$$Q = \Delta n \sum_{i=1}^{\infty} \Delta H_i$$

If only 2:1 complexes are formed it is possible to measure K_2 and $\Delta H_1 + \Delta H_2$ in the following manner. A salt solution (0.08 N) is titrated into a ligand solution (5×10^{-3} N). The formation of the 1:1 complex is complete and only the number of moles of the 2:1 complex formed at the time t, $\Delta n_{2,t}$, is a function of the stability constant K_2:

$$Q_t = \Delta n_1 \Delta H_1 + \Delta n_{2,t} \Delta H_2$$

Such thermograms allow the calculation of K_2 and the sum of ΔH_1 and ΔH_2 [7]. In all titrations it is found that heat effects due to the dilution of salt and ligand solutions are negligible.

An indirect possibility of measuring the sum of the reaction enthalpies $\Sigma_{i=1}^{\infty} \Delta H_i$ for the Ba^{2+} complex with c-BTO is given in the following way. A solution of the cryptand (222) (0.02–0.04 N) is titrated into a solution containing $\mathrm{Ba(ClO_4)_2}$ (5–6×10^{-4} N) and a high excess of c-BTO (2–4×10^{-2} N). Under these experimental conditions the formation of 2:1 or X:1 complexes is complete and the disproportionation reaction (3) with a reaction enthalpy ΔH_{obs} is observed:

$$(222) + \mathrm{ML}^{n+}_x \rightleftharpoons (222\mathrm{M}^{n+}) + x\mathrm{L} \tag{3}$$

Using the separately estimated values for the reaction enthalpy of the cryptand (222) with Ba^{2+} ($\Delta H_{\mathrm{cry}} = -78.2$ kJ mol^{-1} [8]) $\Sigma_{i=1}^{\infty} \Delta H_i$ can be calculated from ΔH_{obs}:

$$\sum_{i=1}^{\infty} \Delta H_i = \Delta H_{\mathrm{cry}} - \Delta H_{\mathrm{obs}}$$

Another experimental method of studying the formation of weak complexes is the NMR technique [9]. This method is easily employed in the study of the 1:1 complex formation between c-BTO and cations. The uncomplexed ligand only shows one resonance for all protons. On adding salts, this signal is shifted to lower fields indicating direct interactions between the ligand molecules and cations. From the knowledge of the chemical shift of the uncomplexed ligand δ_{L} and of the 1:1-complexed δ_{K} the stability constant for the 1:1 complex can be calculated easily from the observed chemical shift δ_{obs}:

$$\delta_{\mathrm{obs}} = (1 - \alpha)\delta_{\mathrm{K}} + \alpha\delta_{\mathrm{L}}$$

$$\text{with } \alpha = \frac{[\mathrm{L}]}{C_{\mathrm{L}}}$$

C_{L} is the initial concentration and [L] the actual concentration of the uncomplexed ligand. During these measurements the ligand (2–12×10^{-3} N) and salt concentration (8–20×10^{-3} N) are varied to ensure 1:1 complex formation. The ^{1}H NMR spectra were run on a Bruker WP-80 Fourier-transform NMR spectrometer using standard software. Internal reference was tetramethylsilane.

Results and Discussion

Calorimetric titrations of alkali, alkaline-earth, and silver salt solutions in methanol with the ligands c-BTO and 9C3 result only in very small temperature changes. Thus, it is impossible to calculate stability constants and reaction enthalpies from the thermograms. Only for the reaction of c-BTO with Ba^{2+} is sufficient heat observed during the titration and a calculation of the complex stability and reaction enthalpy is possible. All experimental values for the reaction between c-BTO, 9C3 and 12C4 in methanol solutions obtained either from calorimetric or NMR measurements are summarized in Table I. The stability constants estimated with different experimental techniques for the Ba^{2+} complex with c-BTO agree with one another very well. Also, the directly and indirectly estimated reaction enthalpies for the formation of a complex between c-BTO and Ba^{2+} with more than one ligand molecule from a calorimetric disproportionate reaction are identical. With the ligand 9C3 Ba^{2+} forms a complex of unknown composition. A 1:1 and 2:1 stoichiometry for 12-crown-4 complexes is well established from the structure of solid complexes [10] and from experimental results obtained in solution [5].

TABLE I. $\log K$ (K in M^{-1}, ΔH (kJ mol^{-1}), and $T\Delta S$ (kJ mol^{-1}) for the Reaction of c-BTO, 9C3, and 12C4 with Bivalent Cations, in Methanol at 25 °C

Ligand	Parameter	Ca^{2+}	Sr^{2+}	Ba^{2+}
c-BTO	$\log K_1$	1.34^a	1.71^a	1.90^a 1.88^b
	$-\Delta H_1$		1.9^b	7.9^b
	$T\Delta S_1$		7.8	2.8
	$\log K_2$			2.45^b
	$\sum_{i=1}^{\infty} -\Delta H_i$			13.8^b 13.8^c
9C3	$\log K_1$	$-^d$	$-^d$	$<1^d$
	$-\Delta H_1$	$-^d$	$-^d$	$-^d$
	$\sum_{i=1}^{\infty} -\Delta H_i$			10.2^b
12C4	$\log K_1$	2.53^e	2.50^e	2.56^e
	$-\Delta H_1$	2.3^e	12.4^e	21.4^e
	$T\Delta S_1$	12.1^e	1.8^e	-6.9^e
	$\log K_2$			2.38
	$-\Delta H_2$	4.3^e	1.6^e	5.7^e
	$T\Delta S_2$			7.8

[a] From NMR measurements. [b] From calorimetric titrations. [c] From a calorimetric disproportionation reaction with the cryptand (222). [d] No detectable heat produced during calorimetric titration; $\log K$ very small or $\Delta H = 0$. [e] From ref. 5.

TABLE II. $\log K$ (K in M^{-1}, ΔH (kJ mol^{-1}), and $T\Delta S$ (kJ mol^{-1}) for the Reaction of c-BTO, 9C3 and 12C4 with Ba^{2+} in Different Solvents at 25 °C

Solvent	Parameter	c-BTO	9C3	12C4
AN[a]	$\log K_1$	3.11^b	$-^c$	4.12
	$-\Delta H_1$	14.5	<2	42.5
	$T\Delta S_1$	3.4		19.1
	$\sum_{i=1}^{\infty} -\Delta H_i$	44.5	14.6	59.5
PC[d]	$\log K_1$	3.28	$-^c$	3.93
	$-\Delta H_1$	16.1	<2	39.5
	$T\Delta S_1$	2.5		17.2
	$\sum_{i=1}^{\infty} -\Delta H_i$	30.9	8.9	63.2

[a] Acetonitrile. [b] From NMR measurements. [c] Not calculable from the thermogram. [d] Propylene carbonate.

Taking into account the observations made in methanol solutions, only the reactions between Ba^{2+} and c-BTO, 9C3 and 12C4 are studied in acetonitrile and propylenecarbonate solutions. Values for the stability constants, reaction enthalpies and entropies are given in Table II.

All three ligands examined are too small to surround Ba^{2+} ($r = 1.36$ Å) [11] or any other cation. The cavity radius in 12C4 is 0.6 Å [12]. A CPK model of 9C3 shows that this ligand does not even possess a cavity. The same is true in the case of c-BTO. In contrast with the crown ethers c-BTO is a rigid molecule. No conformational changes of the ligand during complex formation are possible. Due to the flexible structure of crown ethers the conformation of the free ligand changes during complexation to achieve optimal interactions between all donor atoms and the bonded cation. This process results in negative entropic contributions to the overall reaction entropy. The experimental results clearly show that entropic contributions favour the 1:1 complex formation with the rigid ligand c-BTO compared with 12C4.

The differences in complex stabilities measured in methanol solutions for Ca^{2+}, Sr^{2+}, and Ba^{2+} with c-BTO mainly result from enthalpic changes. Solvation effects for the cations are responsible for this observation. Similar results are obtained for the corresponding 12C4 complexes.

The Ba^{2+} complexes formed in the other solvents studied are more stable compared with the complex stabilities found in methanol solutions. Reduced interactions between the cation and solvent molecules are mainly responsible. As a result observed values of the reaction enthalpy increase since less energy is necessary to partly desolvate the cation during the reaction and the resulting interactions between the ligand donor atoms and Ba^{2+} remain nearly constant in all solvents. On the other hand due to the weaker solvation less solvent molecules are liberated during the complex formation. Thus entropic contributions partly disfavour the reaction between Ba^{2+} and the ligands studied. This explanation is true for the macrocyclic ligand 12C4 because this ligand sets free more than one solvent molecule if it reacts with Ba^{2+}. Due to the rigid structure ot c-BTO and the size of the ligand in all solvents a constant number of solvent molecules is liberated by one ligand molecule. The interactions between c-BTO and solvent molecules obviously are negligible. Therefore, in all solvents studied the values of $T\Delta S$ are nearly constant.

From the measurements of the sum of all reactions enthalpies $(\Sigma_{i=1}^{\infty} H_i)$ no direct conclusion can be drawn about the composition of the complexes formed in solution. However, by comparing the results obtained with c-BTO and 12C4 some very positive predictions are possible.

The sum of all reaction enthalpies is the combination of the reaction enthalpy for the formation of a 1:1, 2:1 (ratio of ligand to cation), 3:1 complex and so on. Up to now, the ligand 12C4 is known to exclusively form 1:1 and 2:1 complexes. In all solvents the values of the reaction enthalpy for the 2:1 complex are smaller compared with the reaction enthalpy for the 1:1 complex formation.

On the assumption that none of the reaction enthalpies is close to zero the approximate composition of the complex formed is obtained by dividing the sum of the reaction enthalpies by the reaction enthalpy for the 1:1 complex formation. Thus, one expects that in methanol and propylenecarbonate solutions 1:1 and 2:1 complexes are formed. In acetonitrile solutions the experimental results even indicate the formation of a 3:1 complex.

In solution the composition of the complexes formed with c-BTO mainly depends on the strength of solvation of the complexed cations. Therefore, in other solvents further different compositions may be found.

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