

Complexation Thermodynamics of Imine-Type Bis(benzocrown ether)s. Part I. Sandwich Complexation of K^+ , Rb^+ , Cs^+ and Tl^+ with Polymethylene and *m*-Phenylene Bridged Carbonylhydrazones of 4'-Formylbenzo-15-crown-5

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Abstract. The complexation thermodynamics of polymethylene and *m*-phenylene bridged carbonylhydrazones of 4'-formylbenzo-15-crown-5 with K^+ , Rb^+ , Cs^+ and Tl^+ was investigated by spectrophotometric titrations in methanol at 283–313 K. The carbonylhydrazone sequences in the bridge of the bis(benzocrown ether)s are optical sensors for the sandwich complexation of metal ions. Within the homologous series of polymethylene bridged carbonylhydrazones a stability peak was found for the sandwich complexes of the 'propylene bridged' compound with K^+ , Rb^+ and Tl^+ . The potassium complex of this ligand shows the highest stability constant compared to all other known bis(benzo-15-crown-5) complexes with K^+ in methanol.

In terms of thermodynamics the formation of intramolecular sandwich complexes is driven by a gain of enthalpy. The unusual high gains of enthalpy and losses of entropy on formation of the most stable sandwich complexes allow us to propose an additional stabilization of the sandwich arrangement by intramolecular hydrogen bridge bonds. The $\Delta H^\circ - T\Delta S^\circ$ diagram gave an excellent straight line allowing discussion of the enthalpy-entropy compensation effect at these complexation reactions.

Key words: bis(benzo-15-crown-5 ether)s, potassium, rubidium, caesium, thallium(I), complexation, thermodynamics, spectrophotometry.

1. Introduction

Bis(crown ether)s are well known to bind a cation larger than the hole size of the crown unit as a sandwich structure [1–7]. They therefore show remarkable enhancement of complexation and change of selectivity compared to corresponding monocyclic crown ethers [1–8]. The high selectivity toward particular cations, the medium stabilities of sandwich complexes and the relative high rates of trapping and release of cation lead to the application of bis(crown ether)s as neutral carriers in ion-selective electrodes [9–13].

Lockhart *et al.* observed that the UV spectra of bis(benzo-15-crown-5 ether)s with azomethine groups in their linking chain show characteristic alteration in the

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presence of KBr or RbBr in methanol [4]. In order to use azomethine groups as optical sensors for complexation reactions we synthesized a hydrolytically stable homologous series of polymethylene bridged carbonylhydrazones of 4'-formylbenzocrown ethers [14]. We have investigated the extracting properties of these new bis(benzocrown ether)s [15] and tested them as neutral carriers in ion-selective electrodes [13].

We now wish to report on our spectrophotometric investigation of the complexation thermodynamics of these imine-type bis(benzo-15-crown-5 ether)s with K^+ , Rb^+ , Cs^+ and Tl^+ in methanol. Independent of our work Inoue *et al.* obtained the first thermodynamic parameters for the complexation of bis(benzo-12-crown-4 ether)s with Na^+ [16] and of a series of polymethylene bridged bis(benzo-15-crown-5 ether)s with K^+ [17] and Tl^+ [16] in methanol/water (80/20 vol.%) by calorimetric measurements and discussed the enthalpy-entropy compensation effect [16–19].

2. Experimental

Bis(benzocrown ether)s **1–9** and the substituted benzo-15-crown-5 **10** (Figure 1) were prepared as described earlier [14]. KCl, RbCl, CsCl and $TlNO_3$ were used in p.a. quality (Merck) and dried under vacuum prior to use. Methanol was refluxed over magnesium turnings and then distilled. Stability constants at 283–313 K were determined by spectrophotometric titrations using a Specord M40 UV-vis spectrophotometer (Carl Zeiss). A salt solution (3 mM) was titrated continuously in a ligand solution (0.03 mM) to a 20-fold excess of salt. Three independent measurements were carried out at the wavelengths of maximal changes in absorbancy due to the complexation. Experimental values for three wavelengths were used together to calculate the complex stability constants by a nonlinear least-squares method [20]. The enthalpy and entropy changes, ΔH° and $T\Delta S^\circ$, were calculated from the slope and the intercept of the linear relationship between $\log K$ and the inverse of the absolute temperature using the equations $\Delta G^\circ = -2.303 RT \log K$ and $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$. Figure 2 shows the $T^{-1} - \log K$ diagram for the complexation of K^+ by the bis(benzo-15-crown-5 ether)s **1**, **3**, **5** and **7**. The correlation coefficients of the regression lines obtained for all 1 : 1 (cation : ligand) complexations are higher than 0.995. In each case the errors in determining the thermodynamic parameters by the van 't Hoff plots including the standard deviations of the $\log K$ values are lower than 4% for ΔH° and lower than 6% for $T\Delta S^\circ$ values.

3. Results and Discussion

3.1. COMPLEX STABILITY CONSTANTS

The UV spectra of the imine-type bis(benzo-15-crown-5 ether)s **1–8** show a characteristic transition band of the conjugated aromatic and azomethine chromophores.

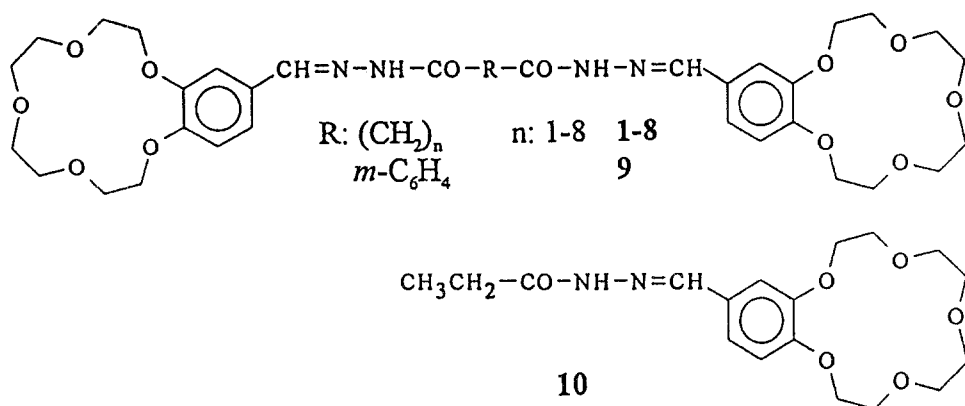
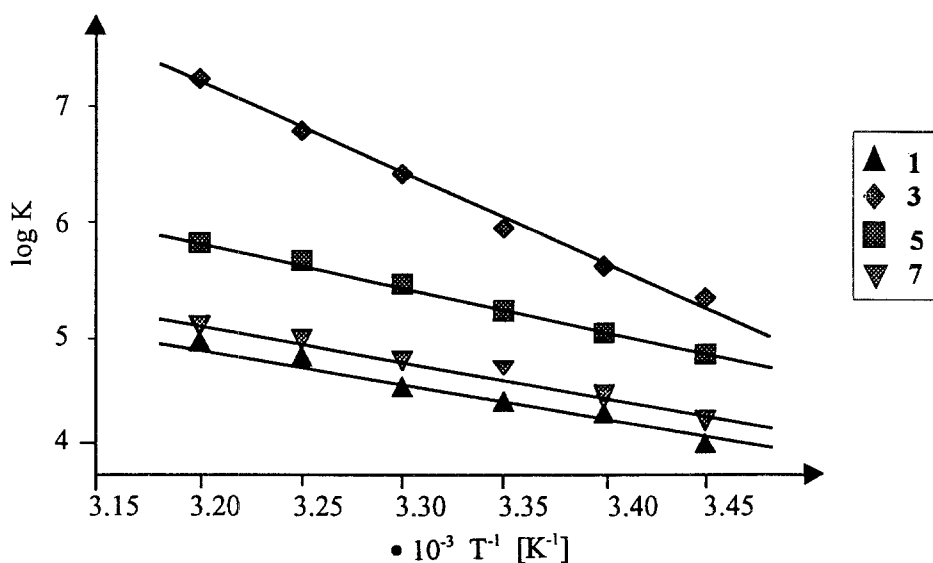


Fig. 1. Ligands studied in this paper.

Fig. 2. $T^{-1} - \log K$ plots for the complexation of K^+ by the bis(benzo-15-crown-5 ether)s 1, 3, 5 and 7 in methanol.

This absorption band has fine structures with two maxima at 292 nm ($\log \epsilon$ ca. 4.62) and 315 nm ($\log \epsilon$ ca. 4.65) as well as two shoulders similar to that shown in Figure 3 for the bis(benzo-15-crown-5) 3. The addition of KCl, RbCl, CsCl or TlNO_3 to a solution of these bis(benzo-15-crown-5 ether)s in methanol causes a hypsochromic shifting of the absorption maxima and a decrease in absorbancy [21]. The largest change was observed when adding equimolar KCl to a solution of ligand 3 (0.03 mM) in methanol, isosbestic points being observed at 248 and 284

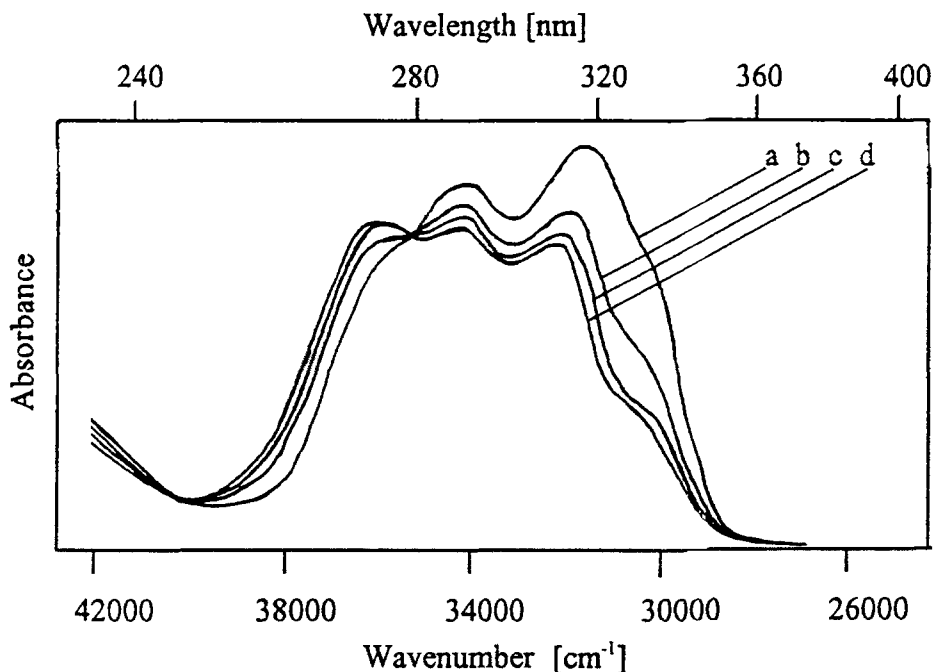


Fig. 3. Optical shifts during the complexation of K^+ by the bis(benzo-15-crown-4) **3** in methanol ($c(\mathbf{3}) = 0.03$ mM); $c(K^+)/c(\mathbf{3})$: (a) 0, (b) 0.5, (c) 1.0, (d) 2.0.

nm. Higher mole ratios of KCl to ligand **3** do not alter the spectrum further (Figure 3). The other complexation reactions being studied are accompanied by similar but smaller changes of the ligand spectra. All spectrophotometric titration curves exhibit a '1 : 1' complex formation similar to that shown for the complexation of K^+ by the bis(benzo-15-crown-5) **3** (Figure 4). In contrast to these observations, no spectral changes occur with addition of KCl, RbCl, CsCl or $TlNO_3$ to methanolic solutions of the corresponding substituted benzo-15-crown-5 ethers, such as **10**. The complexation of size-fitted Na^+ by the substituted benzo-15-crown-5 **10** is merely accompanied by a small decrease of absorbancy (ca. 2%). We therefore conclude that the optical shifts caused by the electronic effects upon cation binding are comparatively small. Most of the hypsochromic shifting of the absorption maxima and the decrease in absorbancy on the formation of sandwich complexes between K^+ , Rb^+ , Cs^+ and Tl^+ and the bis(benzo-15-crown-5 ether)s **1-8** should be a result of electronic effects arising from conformational changes of the conjugated chromophoric sequences, intensive dipole-dipole interactions of the chromophoric systems [22] and the formation of intramolecular hydrogen bridge bonds between the carbonylhydrazone fragments in the sandwich complex structures compared to the uncomplexed bis(benzocrown ether)s.

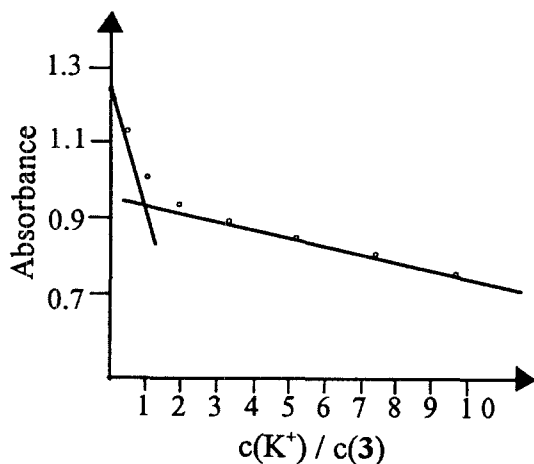


Fig. 4. Titration curve for the 1 : 1 (K^+ : ligand) complexation with the 'propylene bridged' bis(benzo-15-crown-5) **3** in methanol at 318 nm (cut-out).

The '*m*-phenylene bridged' bis(benzo-15-crown-5) **9** has a broad absorption band with one maximum at 328 nm ($\log \epsilon$ ca. 4.74). In the presence of K^+ , Rb^+ , Tl^+ or Cs^+ the intensity of this band decreases and a small hypsochromic shift of the absorption maximum is observed, but isosbestic points do not occur. Whereas the titration diagram for the reaction of ligand **9** with K^+ exhibits a 1 : 1 complexation the corresponding curves for the reactions with Rb^+ and Tl^+ show a successive 1 : 1/2 : 1 (cation : ligand) complexation similar to that shown for the complexation of Rb^+ by the *m*-phenylene bridged carbonylhydrazone **9** (Figure 5). In the case of Cs^+ spectral changes are too small to calculate $\log K$ values for the reaction with ligand **9**.

The values of $\log K$, ΔH° and $T\Delta S^\circ$ for the complexation of K^+ , Rb^+ , Cs^+ and Tl^+ by the ligands **1–9** in methanol are summarized in Table I. Independent of the length of the linking chain in the bis(benzo-15-crown-5 ether)s **1–8** the stability constants of their sandwich complexes decrease in the order $K^+ > Rb^+ > Tl^+ > Cs^+$ (Table I, Figure 6). A stability peak was found for the complexes of K^+ , Rb^+ and Tl^+ at the 'propylene bridged' compound **3**, whereas the stability constants of the Cs^+ complexes hardly vary with the length of the polymethylene bridge in the order of the homologues **1–8** (Figure 6). Compared to all other K^+ complexes of bis(15-crown-5) ligands the complex of the glutaric acid derivative **3** with K^+ shows the highest stability [23]. CPK models show that the bridge in the 'propylene bridged' bis(benzo-15-crown-5) **3** has an optimal length and flexibility to achieve a parallel arrangement of the polyether rings to complex the cations.

The substitution of the flexible polymethylene bridge by a rigid arylene fragment in the case of the *m*-phenylene bridged carbonylhydrazone **9** causes a decrease in the $\log K$ values of the corresponding complexes of up to two orders of magnitude.

TABLE I. Equilibrium constants $\log K$ and thermodynamic parameters ΔH° , ΔG° and $T\Delta S^\circ$ in kJ/mol for the complexation of K^+ , Rb^+ , Cs^+ and Tl^+ by the bis(benzo-15-crown-5 ether)s **1-9** in methanol at 298 K.

Ligand	Cation	$\log K$	$-\Delta H^\circ$	$-\Delta G^\circ$	$T\Delta S^\circ$
1	K^+	4.58 ± 0.02	68	27	-41
2	K^+	5.19 ± 0.02	66	30	-36
3	K^+	6.42 ± 0.05	152	37	-115
4	K^+	5.63 ± 0.02	88	32	-56
5	K^+	5.47 ± 0.01	73	31	-42
6	K^+	5.25 ± 0.02	69	30	-39
7	K^+	4.81 ± 0.01	62	28	-35
8	K^+	4.94 ± 0.02	67	28	-38
9	K^+	4.12 ± 0.03	79	24	-55
1	Rb^+	4.22 ± 0.03	41	24	-17
2	Rb^+	4.51 ± 0.01	66	26	-40
3	Rb^+	5.02 ± 0.04	77	29	-48
4	Rb^+	4.69 ± 0.01	65	27	-38
5	Rb^+	4.47 ± 0.01	52	26	-26
6	Rb^+	4.42 ± 0.01	50	25	-25
7	Rb^+	4.21 ± 0.02	42	24	-18
8	Rb^+	4.22 ± 0.02	54	24	-30
9	Rb^+	3.87 ± 0.18	-	-	-*
		$(7.15 \pm 0.23^{**})$	-	-	-*
1	Cs^+	3.75 ± 0.04	15	21	7
2	Cs^+	3.43 ± 0.04	12	20	8
3	Cs^+	3.53 ± 0.03	43	20	-23
4	Cs^+	3.58 ± 0.04	-	-	-*
5	Cs^+	3.26 ± 0.03	51	19	-32
6	Cs^+	3.48 ± 0.05	-	-	-*
7	Cs^+	3.58 ± 0.06	-	-	-*
8	Cs^+	3.53 ± 0.05	90	20	-70
9	Cs^+	-***	-	-	-
1	Tl^+	4.16 ± 0.01	45	23	-21
2	Tl^+	4.38 ± 0.01	60	25	-35
3	Tl^+	4.80 ± 0.01	84	27	-57
4	Tl^+	4.48 ± 0.01	67	26	-41
5	Tl^+	4.25 ± 0.01	66	24	-42
6	Tl^+	4.14 ± 0.02	55	24	-31
7	Tl^+	3.85 ± 0.02	55	22	-33
8	Tl^+	4.05 ± 0.02	54	23	-31
9	Tl^+	3.88 ± 0.11	-	-	-*
		$(7.82 \pm 0.08^{**})$	-	-	-*

* High standard deviations of the $\log K$ values at different temperatures do not allow the determination of thermodynamic parameters.

** Equilibrium constant for the reaction $2 M^+ + BCE \rightleftharpoons (M_2 BCE)^{2+}$; (BCE = bis(crown ether)).

*** Spectral changes are too small to calculate $\log K$ values for this reaction.

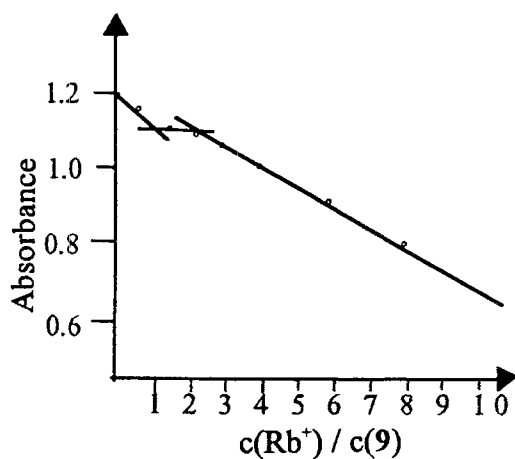


Fig. 5. Titration curve for the successive 1 : 1/2 : 1 (Rb^+ : ligand) complexation with the 'm-phenylene bridged' bis(benzo-15-crown-5) **9** in methanol at 331 nm (cut-out).

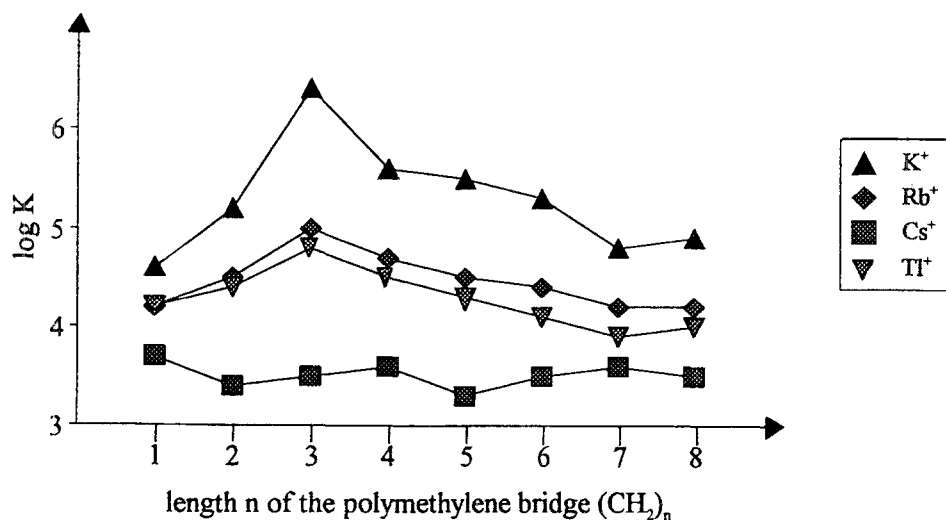


Fig. 6. Dependence of the stability constants $\log K$ of the complexes with K^+ , Rb^+ , TI^+ and Cs^+ on the length of the polymethylene bridge $(\text{CH}_2)_n$ in the bis(benzo-15-crown-5 ether)s 1-8.

The stability constant of the 1 : 1 complex between bis(benzo-15-crown) **9** and K^+ ($\log K = 4.12$, Table I) does not considerably exceed the corresponding value for benzo-15-crown-5 in methanol ($\log K = 3.93$ [24]). The tendency of sandwich complex formation further decreases with increasing cation diameter. In contrast to the complexation of K^+ an excess of Rb^+ or TI^+ causes the formation of

2 : 1 (cation : ligand) complexes with the bis(benzo-15-crown-5) **9**. The value $\log K = 3.87$ (Table I) of the Rb^+ -complex of bis(benzo-15-crown-5) **9** is slightly lower than the stability constant of the corresponding complex of benzo-15-crown-5 ($\log K = 3.97$ [24]). This results in the conclusion that no sandwich complex is formed between the 'm-phenylene bridged' bis(benzo-15-crown-5) **9** and Rb^+ , but only external 1 : 1 and 2 : 1 (Rb^+ : ligand) complexes (Table I). Tl^+ and Rb^+ have nearly identical cation diameters [25], but the higher polarizability of Tl^+ [26] causes lower stabilities of the thallium(I) complexes compared to the corresponding complexes with Rb^+ (Table I).

3.2. THERMODYNAMIC PARAMETERS

The changes of the free enthalpy ΔG° on formation of intramolecular sandwich complexes between the bis(benzo-15-crown-5) compounds **1–8** and K^+ , Rb^+ , Cs^+ and Tl^+ originate in a gain of enthalpy (Table I), which is in agreement with the results of Inoue *et al.* for the complex formation reactions of different bis(benzo-15-crown-5 ether)s with K^+ and Tl^+ in methanol/water (80/20 vol.%) [16]. Figure 7 shows that the appreciable losses of entropy, $T\Delta S^\circ$, are surpassed by gains of enthalpy $-\Delta H^\circ$. The enthalpy and entropy terms of the reactions with K^+ , Rb^+ and Tl^+ follow the course of the corresponding $\log K$ values (Figures 6 and 7).

The formation of the most stable sandwich complexes is accompanied by the highest gains of enthalpy and losses of entropy (Table I). This result is very unusual. Inoue *et al.* found with several series of polymethylene bridged bis(benzo-15-crown-5 ether)s that the formation of the most stable sandwich complexes is always driven by high gains of entropy which surpass the losses of enthalpy compared to corresponding complexes of lower stability [16]. These gains of entropy mainly result from a nearly complete desolvation of the cation in an optimal sandwich arrangement as well as from small conformational changes of the ligand during the complexation. In the case of the polymethylene bridged carbonylhydrazones of 4'-formylbenzo-15-crown-5 ethers **1–8** the formation of intramolecular hydrogen bridge bonds between the hydrazone fragments of the bridging sequences would explain the unusual high gains of enthalpy and losses of entropy. CPK models show that intramolecular hydrogen bridge bonds between NH and C = O [21] or NH and C = N could stabilize the sandwich arrangement of the bis(benzocrown ether)s **1–8**. Additional bonding energies would result in high enthalpy values, while the increasing rigidity of the bridging sequence would decrease the degrees of freedom of the ligand during the complexation and lead to additional losses of entropy. The attempt to grow crystals suitable for X-ray analysis of the complexes between K^+ and the bis(benzo-15-crown-5 ether)s **1–8** has been unsuccessfully to date. We thus need to prove the existence of intramolecular hydrogen bridge bonds by spectroscopic methods.

Because of their long bridging sequence all the representatives **1–8** are able to reach a parallel arrangement of the crown ether units at a distance of 300–400

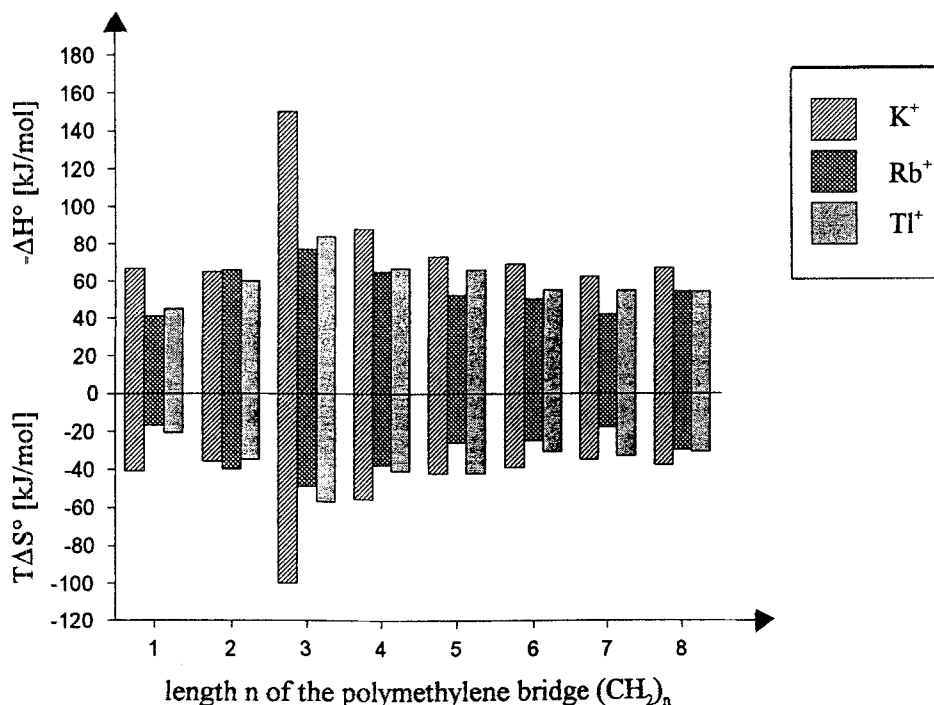


Fig. 7. Gains of enthalpy $-\Delta H^\circ$ and losses of entropy $T\Delta S^\circ$ on the formation of sandwich complexes with K^+ , Rb^+ and Tl^+ as functions of the length of the polymethylene bridge $(CH_2)_n$ in the bis(benzo-15-crown-5 ether)s 1–8.

pm. That is why the contributions of enthalpy and entropy from the desolvation of cations to the energy balance of the sandwich complex formation should be nearly identical. On the contrary different contributions from the desolvation of the bis(benzocrown ether)s and the solvation of the sandwich complexes are more likely due to their different possibilities of forming intermolecular hydrogen bridge bonds with methanol depending on the steric arrangement of their bridging sequences containing hydrazone fragments. While the stability constants of the Cs^+ complexes of the bis(benzocrown ether)s 1–8 lie in the relatively small range of 3.29–3.75, the reaction enthalpies $-\Delta H^\circ$ and entropies $T\Delta S^\circ$ increase with a longer polymethylene chain (Table I). In comparison to K^+ , Rb^+ and Tl^+ the larger Cs^+ achieves more favourable cation-dipole interactions with bis(benzocrown ether)s containing a longer polymethylene chain. Because of the low electrostatic interactions between the large Cs^+ and the benzo-15-crown-5 units of the bis(crown ether)s the increasing losses of entropy originating from an extension of the polymethylene chain are not exceeded enough by gains of enthalpy to realize a stability peak for instance at the 'heptylene bridged' bis(benzo-15-crown-5) 7.

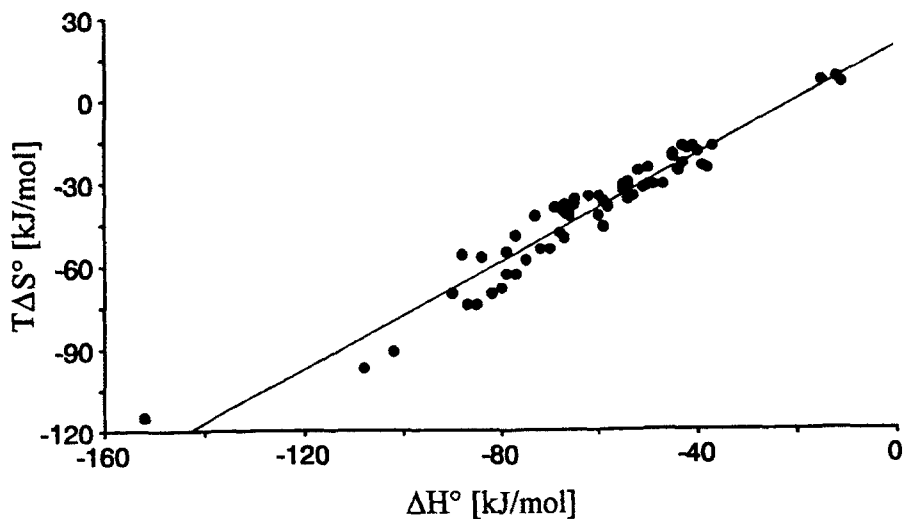


Fig. 8. Enthalpy-entropy compensation for the formation of sandwich complexes between bis(crown ether)s and metal ions using all known thermodynamic parameters from this paper and from [16].

As already emphasized the gains of enthalpy $-\Delta H^\circ$ during the intramolecular sandwich complexation of cations of the bis(benzocrown ether)s **1–8** are mainly compensated by losses of entropy $T\Delta S^\circ$. This enthalpy-entropy compensation was also observed on complexation of cations by other neutral ligands such as podands, coronands, cryptands and natural ionophores [27, 28]. Inoue *et al.* correlated the slope α of the regression line obtained from a $\Delta H^\circ - T\Delta S^\circ$ diagram with the degree of conformational changes of the ligands and the intercept $T\Delta S_0^\circ$ with the desolvation of cations and ligands during the complexation [28]. The $\Delta H^\circ - T\Delta S^\circ$ diagram for the formation of sandwich complexes with the bis(benzocrown ether)s **1–8** gives a straight line ($r = 0.99$) with a slope α of 0.88 and an intercept $T\Delta S_0^\circ$ of 18.1 kJ/mol. These values slightly deviate from those determined by Liu *et al.* for the complexation of K^+ , Tl^+ and Na^+ by bis(crown ether)s in methanol/water (80/20 vol.%) by calorimetry [16, 17] as well as in water/chloroform by solvent extraction [29] ($\alpha = 1.03$, $T\Delta S_0^\circ = 19.23$ kJ/mol, 41 sets of data). Linear regression of all known thermodynamic parameters for the formation of sandwich complexes with bis(crown ether)s in the homogeneous phase (66 sets of data) gives a straight line ($r = 0.97$) with $\alpha = 0.94$ and $T\Delta S_0^\circ = 16.8$ kJ/mol (Figure 8). Because of the larger number of data sets these values of α and $T\Delta S_0^\circ$ are compared with the corresponding values of other neutral ligands (Table II).

The slope α of 0.94 indicates that the degree of conformational changes of bis(crown ether)s during the formation of intramolecular sandwich complexes with cations is comparable with the strong conformational changes of podands and natural ionophores on complexation of cations ($\alpha_{\text{podands}} = 0.86$ and $\alpha_{\text{antibiotics}} =$

TABLE II. Slope (α) and intercept ($T\Delta S_0^\circ$) of the function $T\Delta S^\circ = f(\Delta H^\circ)$ for the complexation reactions with different types of ligands.

Type of ligand	α	$T\Delta S_0^\circ$ [kJ/mol]	r^*	n^{**}	ref.
Podands	0.86	9.6	0.98	151	[19]
Crown ethers	0.76	10.1	0.88	598	[19]
Cryptands	0.51	16.8	0.65	160	[19]
Antibiotics	0.95	23.5	0.91	58	[19]
Bis(crown ether)s	0.94	16.8	0.97	66	***

* Correlation coefficient,

** Number of data sets,

*** Data from [16, 17] and this paper.

0.95). Many podands are converted from a stretched structure to a helical one on cation complexation and several natural ionophores form a coordination sphere only at the cation [30]. Likewise the bis(crown ether)s have to restrict their degrees of freedom considerably to form a sandwich complex with a cation. The same $T\Delta S_0^\circ$ values for bis(crown ether)s and cryptands refer to an almost complete desolvation of the cation by a bis(crown ether), which is comparable to the three-dimensional complexation by cryptands.

Though the thermodynamic parameters leading to the values in Table I have been determined by several methods, in different solvents and with various numbers of complexation reactions of diverse cations this consideration of the thermodynamic parameters ΔH° and $T\Delta S^\circ$ suggested by Inoue *et al.* [19, 28] reflects the similarities and differences on complexation of cations by several classes of macrocyclic ligands.

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