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The complexation properties of new hosts consisting of two crown ethers connected by an anthracene group have been studied using spectrophotometry, fluorescence spectroscopy and cyclic voltammetry. The complexation and recognition properties of these ligands depend significantly on alkyl substituents at the 9- and 10-position of the anthracene group and are also strongly influenced by the solvent. The highest complexation constants with sodium and thallium cations in dimethylformamide were found for ligands with heptyl and ethyl groups. From spectrophotometric titration data it is evident that both crown ether rings participate in formation of complexes with sodium and potassium cations in chloroform–methanol. The determined complexation constants show a negative cooperation effect because $K_{M,1}/K_{ML} < 0.25$. The results of fluorescence experiments with the ligand substituted with two ethyl groups show a decrease in ligand fluorescence upon potassium cation addition, which excludes the formation of sandwich complexes, and suggests that these ligands might be suitable for fluorescence potassium sensors.

The recent interest in the anthracene system was triggered mainly by its fluorescence properties, which are widely utilised in *e.g.* the design of luminescent photoinduced electron transfer sensors.^{1,2} Such sensors allow, for example, monitoring of the concentration of inorganic cations and anions in water,³ as well as neutral guests, *e.g.* sugars.⁴ Recently, the interaction of anthracene systems with biological polyanions (DNA, heparine) has also attracted attention.⁵ It has been found that diaminoanthracene derivatives intercalate CT-DNA with high affinity.⁶

Incorporation of the anthracene group into a sensor molecule can be realised in several ways. Appropriate functionalization of crown ethers and cryptands with anthracene derivatives leads to simple anthracene crown ethers⁷ and anthracene cryptands.⁸ Direct synthesis of anthracene crowns based on functionalization of the anthracene group is very difficult.⁹ The preparation of anthracene bicyclic¹⁰ and tricyclic cryptands¹¹ requires multistep syntheses.

An interesting functionalization of an anthracene crown ether has been reported by De Silva *et al.*¹² These authors have noted that the receptors with an incorporated amine group behave as a digital AND gate with respect to protonation and complexation of sodium cations.

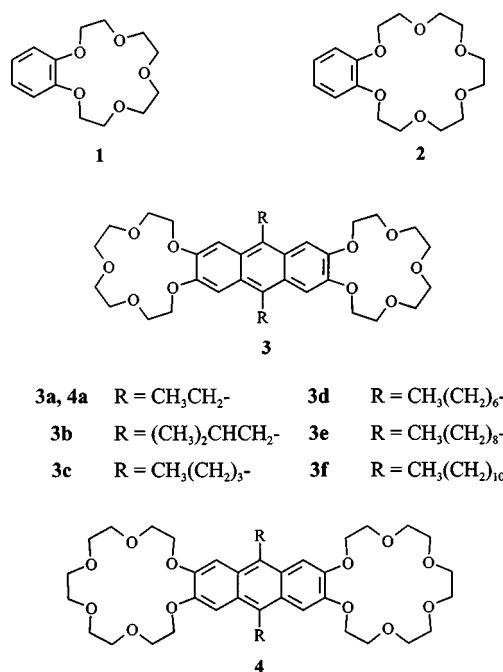
During our studies directed towards the synthesis of new anthracene crowns, we found that upon treatment of benzo-15-crown-5 (**1**) or benzo-18-crown-6 (**2**) with aliphatic aldehydes in the presence of sulfuric acid, the respective anthracene crowns **3** and **4** can be obtained in 15–71% yield.¹³

Since these novel structures consist of two crown ethers connected by an anthracene group, both crown ethers can potentially participate in the formation of complexes with metal cations. The presence of alkyl groups in positions 9 and 10 of the anthracene system can influence the complexation and modify the recognition processes. We decided to investigate the binding properties of several of these new ionophores using electrochemical and spectroscopic techniques.

Results

UV and fluorescence spectroscopy

It is expected that the presence of two crown ether rings in



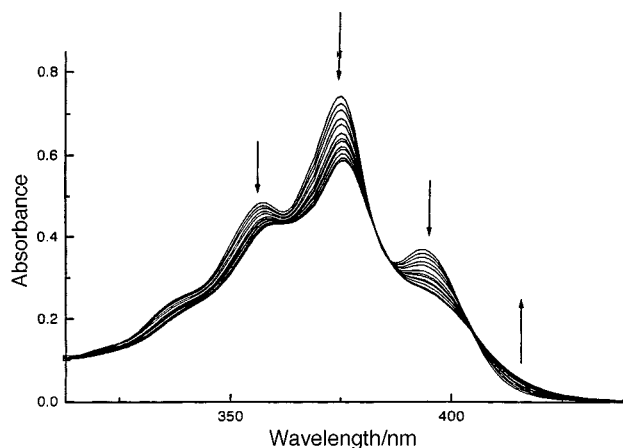
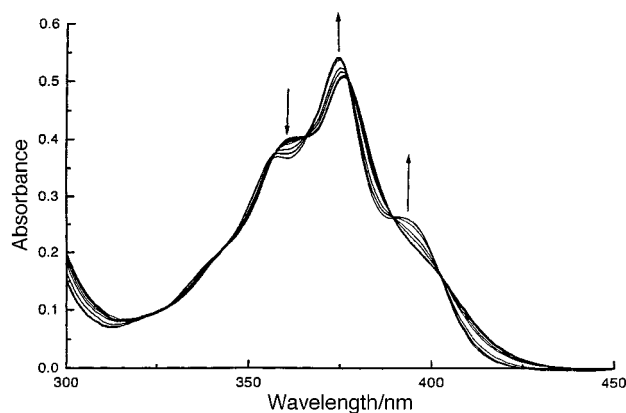
compounds **3** and **4** should influence the overall recognition pattern. The presence of a strong chromophore, the anthracene group, which has a characteristic UV spectrum, facilitates the study of the recognition processes using spectrophotometry. This method was successfully used for the complexation studies of *e.g.* calix[4]arenes¹⁴ and anthracene coronands.¹⁵

Usually, the complexation processes are studied in water or methanol. Unfortunately, the synthesised anthracene crown ethers are poorly soluble in these solvents. A significantly better solubility was observed in chloroform–methanol mixtures, so the spectrophotometric titration of ligand **3b** with potassium thiocyanate was carried out in CHCl_3 –MeOH (8:2 v/v) at room temperature (Fig. 1 and 2).

Upon addition of KSCN to the solution of compound **3b**, the absorbance maximum at 374 nm decreased and a small red shift of this maximum was observed (Fig. 1). The presence of

Table 1 Stability constants determined for sodium and potassium complexes of anthracene crown **3** in chloroform–methanol (8:2 v/v) mixture^a

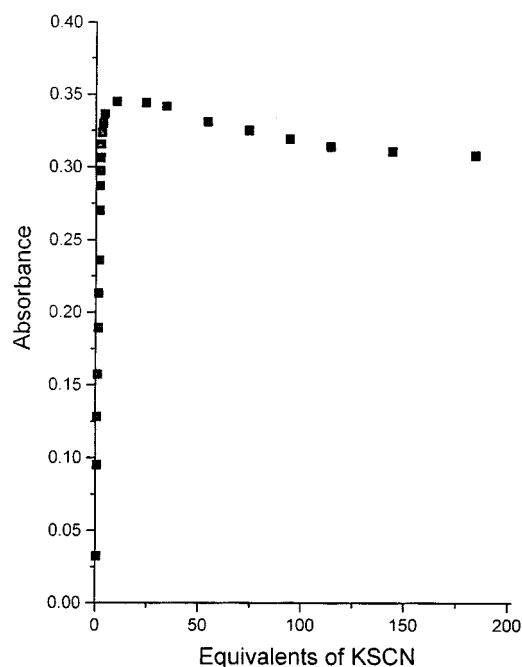
Entry	Compound	Cation	$\epsilon_1^b/\text{mol}^{-1} \text{ dm}^3$	$\log K_{ML}$	$\epsilon_2^b/\text{mol}^{-1} \text{ dm}^3$	$\log K_{M_2L}$
1	3a	Na ⁺	8560	4.40	6850	1.94
2	3a	K ⁺	5740	5.65	6605	2.27
3	3b	Na ⁺	10880	4.62	10620	3.67
4	3b	K ⁺	8150	4.87	9360	2.27

^a At 20 °C. ^b For $\lambda = 375 \text{ nm}$.**Fig. 1** Change in the absorption spectrum of a $6.86 \times 10^{-5} \text{ M}$ solution of crown **3b** in chloroform–methanol (8:2 v/v) upon increasing the concentration of KSCN ($0 < C_{K^+} < 1.66 \times 10^{-3} \text{ M}$).**Fig. 2** Change in the absorption spectrum of a $6.86 \times 10^{-5} \text{ M}$ solution of crown **3b** in chloroform–methanol (8:2 v/v) upon increasing the concentration of KSCN ($1.17 \times 10^{-3} < C_{K^+} < 9.7 \times 10^{-3} \text{ M}$).

two isosbestic points at 385 and 415 nm, clearly visible in the spectrum, indicates the presence of an equilibrium involving at least two absorbing species in the solution, *i.e.* the free ligand and a 1:1 complex. Higher-order complexes are not visible due to their low concentration. Further addition of potassium thiocyanate increases the relative concentration of a second complex (M_2L), which becomes visible in the spectrum when the potassium cation concentration exceeds $1.166 \times 10^{-3} \text{ M}$ (Fig. 2).

In the spectrum shown in Fig. 2, five well resolved isosbestic points at 357, 368, 378, 386 and 405 nm, together with a hypsochromic shift of the 380 nm band, are clearly visible. A similar change of absorbance of anthracene crowns was reported in the literature for the stepwise binding of the cation and the formation of complexes with 1:1 and 1:2 (crown ether to cation) stoichiometry.¹⁵ The changes of the absorbance at 374 nm upon addition of potassium thiocyanate, presented in Fig. 3, allowed us to determine the complexation constants K_{ML} and K_{M_2L} for the formation of the complexes.

The first complexation constant is measured as $\log K_{ML} = 4.87$. If the concentration of potassium cation is

**Fig. 3** Change in the absorbance at 374 nm upon addition of KSCN ($0 < C_{K^+} < 9.7 \times 10^{-3} \text{ M}$).

increased, the next 1:2 complex predominates. This complex (entry 4 in Table 1, $\log K_{M_2L} = 2.27$) is characterised by a larger extinction coefficient. The complexation constants and molar extinction coefficients of both complexes are presented in Table 1.

Since it is already known that complexation of sodium cation by benzo-15-crown-5 is favoured over potassium cation,¹⁶ the UV titration experiments were also performed for sodium thiocyanate and ligand **3b**. The results obtained are included in Table 1. Again, two complexes of 1:1 and 1:2 (ligand to sodium cation) stoichiometry are formed (entry 3 in Table 1) under the conditions studied. The stability constant for the first complex is slightly lower ($\log K_{ML} = 4.62$) than that for the potassium cation. The complexation of the second sodium cation is characterised by $\log K_{M_2L} = 3.67$, which is higher than the corresponding constant for potassium cation. The molar extinction coefficients for both 1:1 and 1:2 sodium complexes are higher than those for the potassium cation complexes.

Analogous UV titrations were carried out with the sodium and potassium cations and ligand **3a** (Table 1, entries 1 and 2). The complexation of the first sodium cation and the corresponding molar extinction coefficient are slightly lower (entry 1 in Table 1) compared to those for crown **3b** (entry 3). A large substituent effect was observed in the complexation of the second sodium cation and, accordingly, a decrease in the constant by two orders of magnitude ($\log K_{M_2L} = 1.94$) was observed. An enhanced complexation of the first potassium cation by crown **3a** was observed while the second complexation constant was identical, within experimental error, to that of ligand **3b**.

The stability constant calculated for the 1:1 complex of ligand **3a** with potassium is fairly high. Therefore, to make sure that a 2:2 sandwich complex is not formed, a series of fluorescence experiments was carried out. The formation of a 2:2

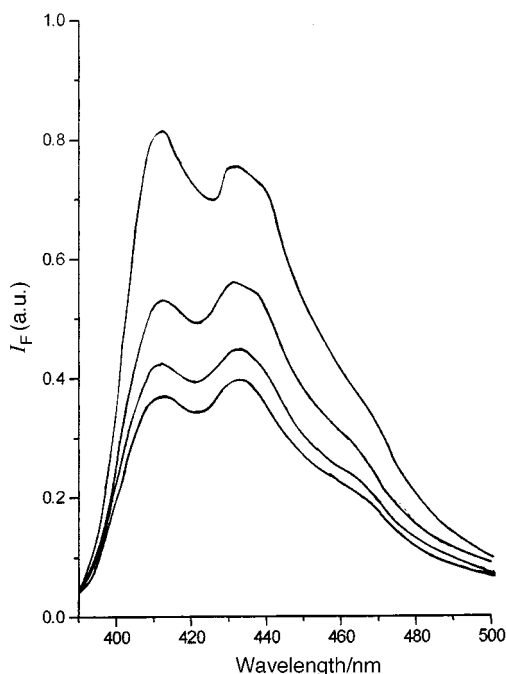


Fig. 4 The decrease of the fluorescence of compound **3a**, recorded at 5.82×10^{-6} M concentration in chloroform–methanol (9:1 v/v), upon addition of KSCN (concentrations 3.33×10^{-6} M, 6.66×10^{-6} M, 1.0×10^{-5} M).

complex should result in a new excimer band in the spectrum. The presence of excimer bands has already been observed upon complexation of cations by anthracene receptors in which two anthracene groups are placed parallel, close to each other.^{2,9,11,16} Since the excimer is poorly fluorescent for a perfect sandwich geometry,¹⁷ the experiments were carried out at different concentrations. Gradual addition of K^+ cations induced a progressive change in the ratio of two highly energetic vibronic bands in the absorption spectra (Fig. 4, chloroform–methanol), but no new excimer band appeared. Also, the stepwise dilution of 1:1 mixtures of ligand **3a** or **3b** and KSCN, from 2.8×10^{-5} down to 2.8×10^{-7} M, simply restored the fluorescence of the free ligand **3a** or **3b**, respectively. No new emission band was observed. We interpret this as evidence that no 2:2 complex is formed in the studied concentration range, and that the dilution simply causes the dissociation of the complex to yield the free ligand and the cation.^{10b}

The decrease of fluorescence of anthracene **3a** upon addition of the potassium cation is promising in terms of possible application in fluorescence chemosensors for potassium.

Voltammetric measurements

For the systematic complexation studies of new ionophores **3** and **4**, we decided to use electrochemical methods. Due to the presence of the anthracene system, the ligand molecules are electroactive and can be selectively reduced in several non-aqueous solvents, *e.g.* DMF. Unfortunately, the reduction peak potentials of the investigated ligands are approximately -2.3 V vs. the reference electrode used, which is close to the reduction potentials of the sodium and potassium cations at mercury electrodes. As a result the peak potential and the peak height cannot be measured quantitatively, as is required for the calculation of the equilibrium constants. The second disadvantage is that the obtained voltammetric peaks of the ligands are irreversible. The irreversibility is probably caused by a follow-up process which is either a dimerization process or a reaction of the radical reduction product with traces of water in the solvent.

A consequence of the above problems is that direct methods of studying the cation binding properties by measuring the

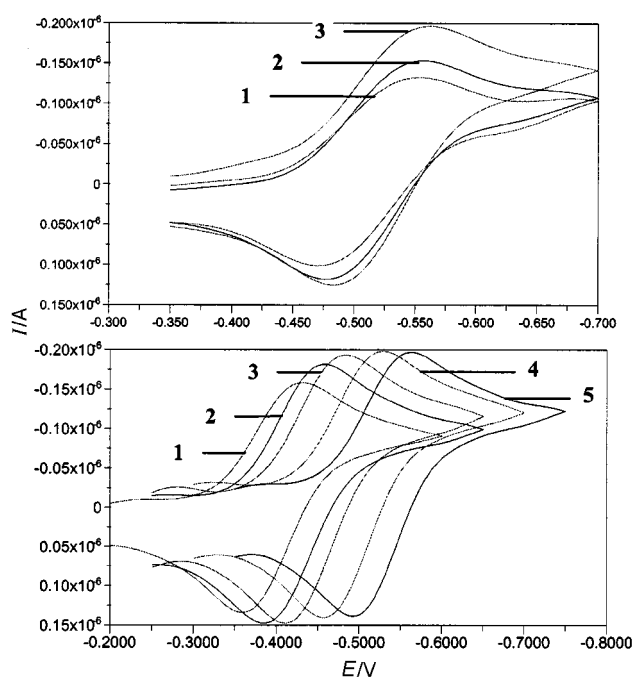


Fig. 5 Upper plot: voltammograms of: (1) uncomplexed Tl^+ ($c = 5 \times 10^{-5}$ M), (2) after addition of ligand **3a** ($c_L = 10^{-4}$ M), (3) ligand concentration 10^{-3} M. Bottom plot: voltammograms of: (1) uncomplexed Tl^+ ($c = 5 \times 10^{-5}$ M), (2) after addition of ligand **4a** ($c_L = 10^{-4}$ M), (3) ligand concentration 3×10^{-4} M, (4) ligand concentration 10^{-3} M, (5) ligand concentration 3×10^{-3} M.

change in the peak potential of either the ligand or the metal cation as a function of the $[M]:[L]$ ratio cannot be used. Therefore, we have turned to an indirect method, in which a competitively complexed cation is introduced and the degree of competition is determined and used to assess the complexation equilibria. The competitive cation (indicator) used in our experiments was thallium(I), which has properties similar to sodium and potassium ions, but its reduction at a mercury electrode takes place at a less negative potential. Accordingly, the $Tl^+/Tl(Hg)$ couple does not interfere with any other electrochemical process in the investigated solutions.

Essentially, in an indirect method, the stability constant of the ligand with the indicator cation is determined, and then the stability constant with Na^+ or K^+ is calculated from the extent of liberation of the indicator cation upon addition of K^+ or Na^+ ions.

Binding of Tl^+ ions. Upon addition of the ligand, the voltammetric reduction peak of the thallium ion shifts toward negative potential. This is behaviour typical of labile complexes with fast exchange of the cation. As might be expected on the basis of cation size, there is a significant difference between the thallium binding by ligands with 15-C-5 and 18-C-6 crowns. Fig. 5 shows the shift of the voltammetric peak potential upon addition of the ligand **3a** and the corresponding shift for **4a**, the latter being significantly larger.

Binding of Na^+ and K^+ ions. For all the ligands, the determination of the stability constants for Na^+ and K^+ ions was done by recording a sequence of voltammograms for free thallium ion (Tl^+), thallium ion with the ligand ($Tl^+ + L$), and thallium ion with the ligand and the competing ion ($Tl^+ + L + Na^+$ or K^+). Fig. 6 shows the corresponding voltammograms for ligands **3a** and **4a**.

The peak potential of the $Tl^+/Tl(Hg)$ couple becomes more negative upon addition of the ligand, then the peaks shift back when the competing ion (sodium or potassium) is added. The general observation was that the competition effect of sodium ions was more pronounced than that of potassium ions, sug-

Table 2 Complex stability constants determined in voltammetric experiments at 20 °C in dimethylformamide. Estimated error *ca.* ± 0.3 $\log K$ units

Entry	Ligand	$\log K_{\text{Tl}^+}$	$\log K_{\text{Na}^+}$	$\log K_{\text{K}^+}$
1	1	1.4	1.6	1.4
2	3a	2.8	1.9	<i>a</i>
3	3b	1.6	0.9	<i>a</i>
4	3c	1.3	2.0	<i>a</i>
5	3d	2.5	3.2	<i>a</i>
6	3e	1.9	<i>a</i>	<i>a</i>
7	3f	2.4	1.9	<i>a</i>
8	4a	4.9	4.4	6.2

a The formation of the respective complex was not observed under experimental conditions.

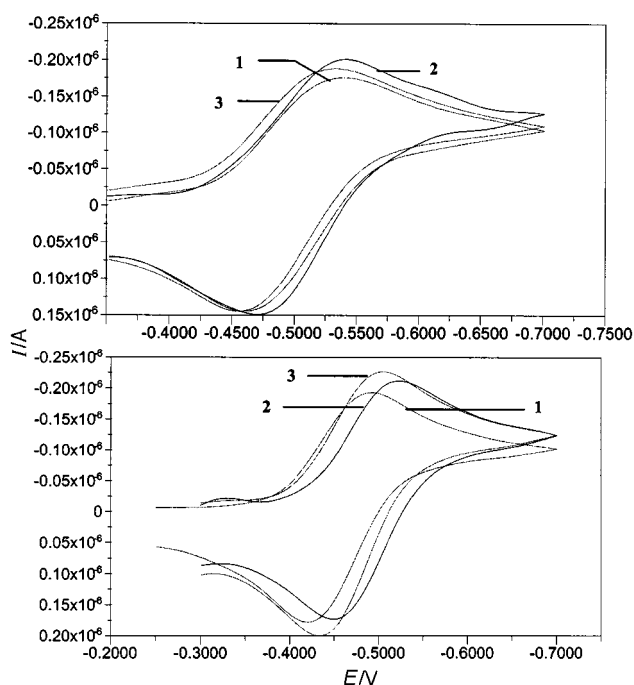


Fig. 6 Upper plot: voltammograms of: (1) uncomplexed Tl^+ ($c = 5 \times 10^{-5}$ M), (2) after addition of ligand **3a** ($c_L = 5 \times 10^{-4}$ M), (3) addition of sodium ions ($c_{\text{Na}^+} = 10^{-1}$ M). Bottom plot: voltammograms of: (1) uncomplexed Tl^+ ($c = 5 \times 10^{-5}$ M), (2) after addition of ligand **4a** ($c_L = 5 \times 10^{-4}$ M), (3) addition of sodium ions ($c_{\text{Na}^+} = 10^{-2}$ M).

gesting that the potassium ions are bound more weakly than sodium ions.

Stability constants. The complex stability constants measured electrochemically for thallium, sodium and potassium cations in dimethylformamide are presented in Table 2.

An inspection of Table 2 reveals that the stability constants of thallium and sodium complexes with anthracene crowns **3** show pronounced dependence on the nature of the 9,10-substituents in the anthracene group. In dimethylformamide, the stability constants of sodium complexes of crown **3a** and **3b** (rows 2 and 3 in Table 2) are smaller than those obtained in CHCl_3 -MeOH (Table 1). The formation of potassium complexes was not detectable in dimethylformamide, while for both crowns the 1:1 complex stability constants in CHCl_3 -MeOH were higher for potassium than for sodium ions. Also, the trend in the stability constants of sodium complexes is reversed. The sodium complex of 1:1 stoichiometry with crown **3b** possessing isobutyl groups in CHCl_3 -MeOH is slightly stronger than that with ethyl groups at the anthracene moiety (entry 1 and 3 in Table 1). In dimethylformamide, this sequence was reversed and the stability constant decreased from $\log K_{\text{ML}} = 1.9$ for compound **3a** to $\log K_{\text{ML}} = 0.9$ for compound **3b**. The use of n-butyl

groups caused an increase in K to a value of $\log K_{\text{ML}} = 2.0$, which is almost equal to that of the ethyl-substituted ligand **3a**. The elongation of the aliphatic groups by three carbon atoms increased the sodium stability constant to $\log K_{\text{ML}} = 3.2$ for compound **3d** (entry 5 in Table 2), but an additional carbon atom decreased the constant so strongly that it was not measurable under the experimental conditions (entry 6 in Table 2). For the last compound studied, **3f**, substituted with dodecyl groups, the measured stability constant with sodium, $\log K_{\text{ML}} = 1.9$, equals the one for crown **3a**, what indicates that the influence of both ethyl and dodecyl alkyl groups on the stability constant is very similar. The modulation effect of the alkyl groups on the stability constants is also observed for the thallium complexes. Again, the highest complexation constant was observed for the heptyl and ethyl groups (entries 2 and 5 in Table 2).

The influence of substituents on the stability constants of benzo-15-crown-5 sodium complexes has been reported in the literature and a good Hammett correlation was found for nine 4'-benzo-15-crown-5 derivatives.¹⁸ Unfortunately, only one alkyl group was studied and the presence of this group caused an increase in the stability constant from $\log K_{\text{ML}} = 3.44$ to 3.96 upon substitution of an H atom by a methyl group. It is interesting to note that no Hammett correlation was found for benzo-18-crown-6. Our results demonstrate that every change of alkyl substituent resulted in a change in the complex stability constants.

The enlargement of the crown ether groups by addition of one ethyleneoxy unit to crown **3b** to obtain crown **4a** caused an increase of the complexation constants for all cations studied (entry 8 in Table 2). The increased number of ethereal oxygen atoms stabilised the complexes formed. The increase in the diameter of the crown ether cavities resulted in their better matching the potassium cation. Therefore, the complexation of potassium is much stronger ($\log K_{\text{ML}} = 6.2$) than in the case of thallium and sodium. Such a selectivity change agrees well with the literature data.¹⁹

An analysis of the spectrophotometric titration data presented in Table 1 leads to the conclusion that both crown ether rings participate in the complexation. The complexation of the first cation can increase or decrease the binding of the second cation. Such a cooperativity in cation binding is of great interest. The positive cooperative effect is present in biological systems.²⁰ The organization of organic compounds in self-assemblies requires positive cooperativity and is less frequently encountered.^{15,21} A model system for studying the influence of cooperative cation binding on transport was designed and it was shown that positive cooperativity reduces transport effectiveness.²²

The complexation constants of sodium by crown **3b** in chloroform-methanol ($\log K_{\text{ML}} = 4.62$ and $\log K_{\text{M,L}} = 3.67$) differ only by one order of magnitude. This system is characterised by a negative cooperation effect, since $K_{\text{M,L}}/K_{\text{ML}} < 0.25$.¹⁵ For compound **3a**, this difference in the complexation constants is even larger for the sodium cation, and is almost the same for the potassium cation. Most probably the negative cooperative effect is caused by two factors. The first one is the electrostatic repulsion between two complexed cations. The second factor is the reorganization of the receptor electron density upon binding of the first cation. This reorganization weakens the interaction of the free crown ether with the second cation. Both effects have already been discussed in the literature.^{15,10b,22}

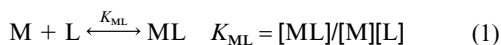
Therefore, it can be concluded that the complexation and recognition properties of the studied anthracene crown ethers significantly depend on the alkyl substituents and are strongly influenced by the solvent.

Experimental

The synthesis of anthracene crowns **3** and **4** has been described previously.¹³ Sodium and potassium thiocyanates were purified

by recrystallisation from methanol. Chloroform was distilled from calcium hydride. Methanol used was analytically pure. The absorption measurements were performed with a Cary 1E spectrophotometer in a quartz cell with 1 cm optical path length at 20 °C (± 0.1 °C). After each addition of the cation, the absorption spectrum was recorded between 270 and 900 nm. Emission spectra were recorded on a Perkin-Elmer MPF-3 in the same cell at room temperature.

The overall binding constants were determined from the variation of absorbance at a fixed wavelength. The overall binding constant for 1 : 2 stoichiometry is defined as a product of the stepwise binding constants K_{ML} and K_{M_2L} [eqn. (1) and (2)].



Two methods were used to determine the K_{ML} and K_{M_2L} constants. The direct change of absorbance upon addition of cation allowed us to calculate K_{ML} . Since K_{M_2L} differs from K_{ML} by at least one order of magnitude, the same procedure was used for K_{M_2L} calculation based on the assumption that only these two complexes are present in the solution. Both complexation constants were also calculated according to the general procedure.¹⁵ In all cases, full compliance of both calculation methods was achieved and the calculated K values differed by less than 3%.

In all electrochemical experiments, dimethylformamide (DMF, Baker Analyzed) was used as solvent. The supporting electrolyte was tetrabutylammonium tetraphenylborate (Fluka, >99%), chosen to avoid any side complexation effects. Metal cations were introduced as solutions of salts: thallium nitrate (TlNO₃, BDH Laboratory Reagent, 0.01 M stock solution), sodium perchlorate (NaClO₄·H₂O, Koch-Light Laboratories, 1 M stock solution), and potassium perchlorate (KClO₄, Xenon, Łódź, 0.1 M stock solution). All solutions were freshly prepared each day.

Voltammetric experiments were carried out using a three-electrode setup. A static mercury electrode (SMDE-1, Laboratorni Pristroje Praha) was used as the working electrode, and a platinum wire was the counter electrode. The reference electrode was an Ag/AgCl electrode filled with 0.1 M solution of tetraethylammonium chloride in methanol. Cyclic voltammograms were recorded using either Autolab (Eco Chemie, Netherlands) or M283 (EG&G, USA) potentiostats. All measurements were performed at 20 °C in a thermostated quartz cell. Solutions were deaerated with argon.

The voltammograms of thallium ions were recorded in the potential range from -0.3 to -0.7 V, at a sweep rate of 0.1 V s⁻¹.

Both coordination numbers and stability constants were determined using a modified version of the DeFord-Hume method.²³ Since the thallium ion behaved in all experiments as an electrochemically reversible system (anodic to cathodic peak separation was in the 60–70 mV range), the original DeFord-Hume method applicable to polarography was adapted. The shifts of polarographic half-wave potentials were replaced by the corresponding shifts of peak potentials. From these shifts and the total concentrations of species in the cell, the functions F_0 were constructed and solved numerically using a program written in the C computer language. The calculation scheme was the following: (i) the value of the experimental complex formation function $F_{0,exp}$ was calculated using the potential shift data; (ii) the equilibrium concentrations were calculated for the assumed stability constant(s), using an appropriate algorithm;²⁴ (iii) the formation function $F_{0,calc}$ was computed from calculated equilibrium concentrations; and (iv) the program iteratively fitted $F_{0,calc}$ to $F_{0,exp}$ by varying the stability

constant(s) and repeating steps (ii)–(iv), according to the algorithm.²⁵

The fitting was finished when the changes in equilibrium concentrations, resulting from the latest correction to the stability constant, were less than 0.1% of the equilibrium concentration value.

In the calculation of the constants determined by the indirect method, the difference in the procedure was that the equilibrium concentration of the electroactive cation [step (ii) in the calculation] depended also on the concentration of the competing ions.

Because the changes in the peak height were small and didn't exhibit any clear trend, it was concluded that the variation of diffusion coefficients was so small that it had a negligible effect on voltammograms. The irregularities were most probably caused by the changes in volume and viscosity of the solution.

In the investigated concentration range, which was limited due to the solubility of the ligands, the stability constants for the complexes with stoichiometry of 1 : 1, 2 : 1, 1 : 2 and 2 : 2 were computed. Except for 1 : 1 stoichiometry, all other stability constants obtained were negative, which indicates that the corresponding complexes were absent from the solution. The higher-order complexes could possibly be formed if a higher concentration of the ligand could be attained.

The computer program for the calculation of the stability constants is available on request from the authors.

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