

Lithium Selective Chromogenic Azocrown Ethers

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Abstract

Novel chromogenic crown ethers having an intraannular azo and phenolic hydroxy subunits have been used as complexing reagents for alkali metal cations. The complex formation was studied by visible spectroscopy and formation constants were calculated. The most pronounced spectral changes were observed for lithium ion.

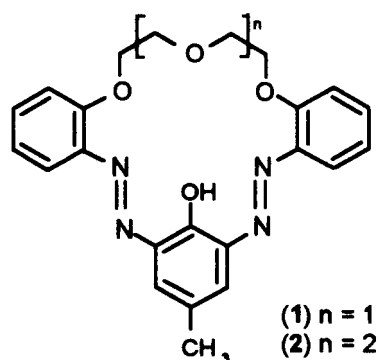
Introduction

In recent years the development of proton dissociable chromogenic crown ether reagents for determination of alkali metal ions has been reported. Chromoionophores discovered by Dix and Vögtle [1] present reagents changing color or fluorescing upon interaction with ions [2]. Since then a variety of proton-dissociable chromogenic crown ethers have been described [3]. In the compounds developed so far, the phenolic hydroxy group is an integral part of the macrocyclic skeleton with chromophores located outside the macrocycle [4, 5]. Other examples of these kinds of compounds are spherands [6] or cryptand-based chromophores carrying an inward-facing phenolic group [7–9] or macrocyclic polyamines bearing an intraannular phenolic group [10]. A short review of the above mentioned compounds is given in [3e].

A problem exists with these compounds in regard to the spectral behavior of anionic forms of such compounds in homogeneous, water-containing solvents. Spectral separations between the hydrated "free" anions and their complexes are usually very small when complexation with alkali metal ions is concerned. These limit applications of chromoionophores for spectrophotometric analysis in essentially all aqueous media [3a].

The inconvenience related to the above spectroscopic properties of the above mentioned chromoionophores has been overcome by placing the azo-chromophores within the macroring of a crown ether. New proton-dissociable crown compounds (**1–2**) resembling mordant azo-dyes have been reported [11], and to the best of our knowledge these compounds are the first to have intraannular azo and phenolic hydroxy subunits.

The azo groups form part of the macrocycle. The phenolic OH group, which is located within the cavity, forms a strong intramolecular hydrogen bond with one of these azo groups. It was expected that cations forming complexes coordinate to phenolate oxygen, to electron donating polyether oxygen atoms of the macrocycle,



and to one of the nitrogen atoms of each azo group [12]. This, in turn, should cause large spectral differences between the chromogenic anion and its cation complex. The predicted participation of the —N=N— chromophore in cation capture inside the crown ether cavity should stabilize the complex formed. The macrocyclic structure of the anion should increase the selectivity of the chromoionophore towards cations of different size. The high selectivity of these systems towards alkali metal cations and especially to lithium has been reported [11].

Lithium is one of the most investigated alkali metals due to its importance in many fields. New Li^+ selective chromoionophores have been designed and used in aqueous media [9, 10, 13] as well as in organic solvent [14, 15].

Our attention in this work was focused on lithium. The goal was to determine whether the novel chromogenic compound can selectively bind lithium ion and under what conditions.

This paper reports UV-visible spectral changes of 18-membered and 21-membered crown ether (**1** and **2**) solutions in the presence and absence of Li^+ , Na^+ and K^+ ions. The solubility of crown ethers in water is very limited and their interactions with these cations are low in aqueous media. The chromoionophores are not sufficiently stable in many solvents; they are stable in solutions of dioxane or diluted

dioxane. These systems were selected for spectrophotometric studies considering also satisfactory solubilities of the interacting salts. The spectra were measured at $\text{pH} > 12$ which optimize the spectral differences. The investigated crowns exhibit high sensitivity for Li^+ , Na^+ and K^+ . The most pronounced spectral changes were observed for Li^+ .

The spectra were measured up to a large excess of cation to crown ether and finally the limiting spectra were obtained. From these spectra the equilibrium constants were estimated.

Experimental

Chromogenic 18-membered (**1**) and 21-membered (**2**) azo-crown ethers have been prepared according to the method described earlier [4]. Dioxane (POCh, Poland) was purified in a typical way and distilled. Triethylamine (POCh) was distilled over potassium hydroxide pellets. Tetraethylammonium hydroxide (POCh, aqueous solution) was used as received.

LiCl , CsCl puriss p.a. (Fluka), NaCl , KCl puriss p.a. (POCh), RbCl p.a. (Aldrich) and $\text{Ba}(\text{ClO}_4)_2$ p.a. (POCh) were dried and kept under vacuum. LiClO_4 p.a. (Aldrich) was vacuum dried at 150° and kept under vacuum.

Spectroscopic measurements were performed at 298 K in quartz cells with a Beckman UV-VIS 5270 spectrophotometer.

Results and discussion

Reactions of crown ethers **1** and **2** with cations in the presence of tetraethylammonium hydroxide

UV-visible spectra of solutions of the novel chromogenic crown ether (**1**) with an excess of alkali metal cations (Li^+ , Na^+ , K^+) have been measured in dioxane–water (1 : 1 v/v) mixtures. The investigated solution was adjusted to above $\text{pH} = 12$ with tetraethylammonium hydroxide to obtain the proper condition for complexation of metal ion. The concentration of crown ether was kept constant (0.025 mM) in all solutions. Absorption spectra of solutions of crown ether **1** showed no absorption maximum in the region around 500 nm. In the presence of alkali metal cations a new absorption band was observed. The chromogenic crown ether gave greater spectral responses to the presence of Li^+ ions than to Na^+ or K^+ . For solutions containing crown ether and lithium cation the maximum absorption was observed at $\lambda_{\text{max}} = 525$ nm; for sodium and potassium ions the maximum of a new absorption band was observed at about $\lambda_{\text{max}} = 549$ nm (Figure 1).

A well pronounced isosbestic point for the system in the presence of lithium ($\lambda = 463$ nm) and sodium ($\lambda = 481$ nm) cations suggested that two absorbing species were present in the solution. The assumed 1 : 1 stoichiometry of the formed complexes with the metal was confirmed by factor analysis [16] of these systems. Based on the factor analysis, the theoretical absorption of the anionic form of the crown ether

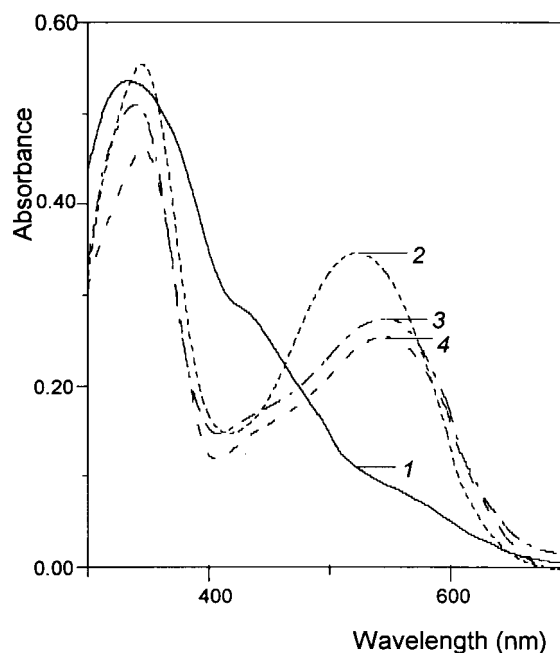


Figure 1. Absorption spectra of azocrown ether **1** – metal salt systems in dioxane–water (1 : 1 v/v) in the presence of Et_4NOH at $\text{pH} = 12$. Crown ether concentration 0.025 mM. (1) salt free; (2) spectrum in the presence of LiCl (0.05 M); (3) KCl (0.2 M) and (4) NaCl (0.2 M).

Table 1. Complex formation constants of azocrown ethers with alkali metal salts in dioxane–water system (1 : 1 v/v) in the presence of different bases: tetraethylammonium hydroxide (Et_4NOH) or triethylamine (TEA)

Salt	18-membered azocrown ether 1 with addition of		21-membered azocrown ether 2 with addition of TEA K (M^{-1})
	TEA	Et_4NOH	
	K (M^{-1})	K (M^{-1})	
LiCl	50.0 ± 2.7	880 ± 21	230.0 ± 3.8
NaCl	14.0 ± 0.5	326 ± 6	123.0 ± 2.0
KCl	5.4 ± 0.4	82 ± 3	51.2 ± 2.5

and its totally lithium or sodium complexed forms were calculated. The percentage of the complexed form of the crown ether in each solution was also calculated. The formation constants of the investigated crown ether with lithium, sodium and potassium have been calculated by the modified Benesi–Hildebrand method [17]. The results are shown in Table 1.

To obtain the crown ether in the anionic form the proper environment is required. Tetraethylammonium hydroxide was used to obtain the appropriate pH in the investigation of the 18-membered crown ether. Addition of tetraethylammonium hydroxide to the crown ether solution in dioxane–water did not modify the electronic spectra. Under these conditions the acidic hydrogen atom was not ionized. This phenolic proton is stabilized inside the macrocyclic cavity by the hydrogen bond involving phenolic hydrogen and nitrogen from the azo group. When alkali metal cation is added to the azocrown ether solution a proton is exchanged with the cation, which results in perturbation of the optical prop-

erties of the chromophore in solution as a consequence of complex formation. This is in agreement with data recently published by Micheloni et al. describing lithium encapsulation by phenolic aza cages with azo chromophores external to the molecular cavity [9]. Better conditions for cation complexation within the cavity could be expected if the proton ionizable group of the chromophore is positioned within a binding site of the ionophores to promote the proton dissociation by metal ion binding. Kimura et al. [10] investigated azacrown ethers with an intraannular phenol group where phenol ionization is promoted by addition of an alkaline earth metal cation. He compared these results with crown ether homologues where basic conditions are needed to displace the phenol proton for M^+ and M^{2+} .

Using tetraethylammonium hydroxide or tetrabutylammonium hydroxide to obtain the appropriate pH in a solution of the 21-membered azocrown ether (**2**) in dioxane–water (1 : 1, v/v) solution is accompanied by formation of a new absorption band at $\lambda_{\max} = 538$ nm. This makes it difficult to use the mentioned bases for the purposes of adjusting pH since the system will be too complex. This is in contrast to the 18-membered azocrown ether (**1**) where the analogous absorption band upon addition of alkylammonium base does not appear [18].

Reactions of crown ethers 1 and 2 with cations in the presence of triethylamine (TEA)

To maintain the appropriate pH condition for the complexation of **2** in solution, triethylamine (TEA) was used instead of tetralkylammonium hydroxides. Spectral changes accompanying complexation of azocrown ethers **1** and **2** with Li^+ , Na^+ , K^+ in dioxane–water solution in the presence of TEA have been measured in order to compare the spectral behaviour of the investigated crown ethers. Absorption changes at λ_{\max} accompanying complexation of the 18-membered azocrown ether (**1**) with the investigated cations are much smaller than for analogous solutions of the 21-membered azocrown ether (**2**) and consequently formation constants are lower [18].

The TEA concentration required to observe color changes during complexation of the crown ether with metal cations was examined. The measured absorbance of crown ether – salt solutions remained constant at the final 3% (v/v) concentration of TEA. The absorption spectra of azocrown ethers (Figure 2) in the presence of TEA before the cation was added showed no absorption band in the region around 500 nm. Addition of TEA to the crown ether solution did not cause deprotonation of the phenolic group but created the appropriate condition for exchange of the hydrogen with the cation when salt was added. Observed formation constants for crown ether–cation complexes depend on pH. Et_4NOH as a stronger base than TEA resulted in higher pH values and better conditions for exchange reaction with metal cation. Both bases withdraw the proton from the phenol group but the species formed in these reactions are different. The protonated TEA can be easily deprotonated but the proton withdrawn by Et_4NOH is converted to H_2O .

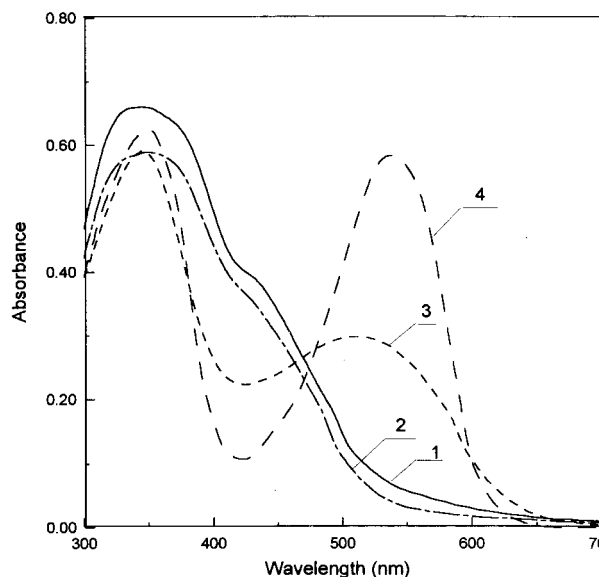


Figure 2. Absorption spectra of 18- and 21-membered azocrown ether–LiCl system in dioxane–water (1 : 1, v/v). Azocrown ether concentration 0.025 mM, TEA (3% v/v). (1) 18-membered crown ether; (2) 21-membered crown ether; (3) 18-membered crown ether with LiCl and (4) 21-membered crown ether with LiCl; salt concentration in both cases 0.1 M.

The addition of lithium (as well as sodium and potassium) chloride to a crown ether solution created a new absorption band at $\lambda_{\max} = 538$ nm (Figure 2). The spectra were measured up to high cation to crown ether ratios and the limiting spectra were obtained. A well pronounced isosbestic point for the system containing lithium suggests the presence of two absorbing species at equilibrium (1 : 1 complex stoichiometry), which was confirmed by factor analysis. The formation constants for this system were found as above using the modified Benesi–Hildebrandt method [17]. The theoretical absorption of the anionic form of the crown ether and the absorption of the totally complexed crown ether were calculated using factor analysis [16].

Sodium or potassium chloride added to the azocrown ether (**1**) solution in the dioxane–water–TEA system also creates a new absorption band at $\lambda_{\max} = 538$ nm but the absorption changes are smaller than in the presence of lithium chloride. Rubidium or cesium salts added to the solution of azocrown ether (**1**) in dioxane–water–TEA do not cause formation of a new absorption band in the mentioned region.

The intensity of the new spectral band formed upon the addition of the same cation to the solution of 18-membered or the 21-membered crown ethers is greater in the case of the 21-membered crown ether (Figure 2). The surprising, higher values of formation constants for the crown with the larger cavity might be caused by possible coordination of the lithium ion with a water molecule that fits better in its cavity.

In the measured water–dioxane solvent system the new absorption band formed upon complexation with selected cations is observed only at appropriate pH conditions, indicating that TEA or tetraalkylammonium hydroxide is required for complexation to occur. No spectral changes are observed in the absence of these bases.

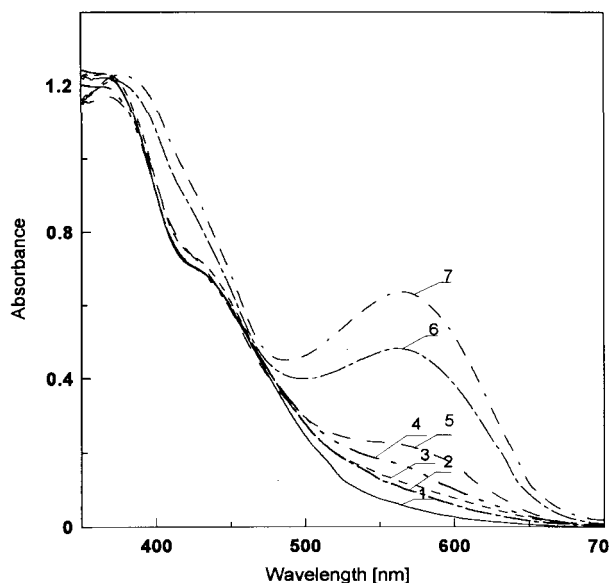


Figure 3. Absorption spectra of 18-membered azocrown ether–LiClO₄ system in pure dioxane. Azocrown ether concentration 0.058 mM. (1) Salt free; (2) 0.017; (3) 0.08; (4) 0.17; (5) 0.34; (6) 1.68; (7) 7.6 mM of LiClO₄.

Reactions of crown ethers **1** and **2** with cations in pure dioxane

Different properties of the crown ether–salt systems are observed in pure dioxane solution. The investigated azocrown ether **1** or **2** solutions showed a characteristic color change when lithium salt was added without addition of base to the dioxane solution. The color changed dramatically from yellow to pink even in the presence of traces of lithium salts; the new absorption band appeared at about $\lambda_{\max} = 566$ nm and $\lambda_{\max} = 538$ nm for the 18-membered and 21-membered azocrown ether respectively. Changes in absorption spectra are caused by coordination of lithium ion to phenolic oxygen enhanced by interactions with nitrogen from the azo group and oxygen from the polyether ring. The spectral changes are more pronounced for the 18-membered azocrown ether (Figure 3). The formation constant for the 18-membered crown ether **1** and LiClO₄ in dioxane, estimated according to the Benesi–Hildebrandt method, is equal to $1330 \pm 60 \text{ M}^{-1}$. LiClO₄ was used instead of LiCl because of its increased solubility in dioxane. The higher value of the complex formation constants might be due also to differ solvation properties of aqueous and organic media.

The complexation reaction in pure dioxane is characteristic for lithium ion and is not observed for any other alkali metal cation. This behavior has possible application in analytical purposes to identify small amounts of lithium. An 18-membered crown ether solution at 0.058 mM added to a solution of LiClO₄ at 0.017 mM results in observable spectral changes (see spectra).

The complexing abilities of compound **2** were also checked towards divalent cations like strontium, calcium, nickel and barium. The preliminary data in pure dioxane without addition of base show that only barium salt added to a solution of **2** creates a new band with a maximum at longer wavelength ($\lambda_{\max} = 588$ nm).

Novel chromogenic azocrown ethers were investigated and appear to be good complexing agents for lithium, sodium and potassium in the dioxane–water system. For analytical purposes the most promising feature seems to be specific complexation of lithium ion by the novel chromogenic crown ethers in pure dioxane

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