Supramolecular Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

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To cite this Article Inerowicz, Halina D. , Skwierawska, Anna and Biernat, Jan F.(2000) 'Novel Chromogenic 21-Membered Azocrown Ether Lithium Selective Reagent', Supramolecular Chemistry, 12: 1, 111 — 114
To link to this Article: DOI: 10.1080/10610270008029810
URL: http://dx.doi.org/10.1080/10610270008029810

SUPRAMOLECULAR CHEMISTRY, Vol. 12, pp. 111-114
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the Harwood Academic Publishers imprint,
part of the Gordon and Breach Publishing Group.
Printed in Malaysia

Novel Chromogenic 21-Membered Azocrown Ether Lithium Selective Reagent

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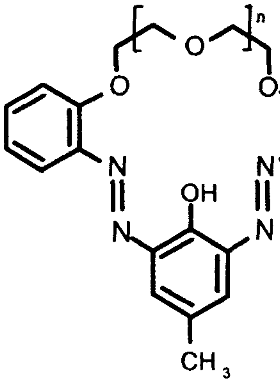
Novel chromogenic 21-membered crown ether having an intraannular azo and hydroxy subunits has been used as a complexing reagent for alkali metal cations. The complex formation was detected by visible spectroscopy and formation constants were calculated. The most pronounced spectral changes were observed for lithium ion.

Keywords: Chromogenic reagent, azocrown ether, lithium complexation, formation constants

During last years the development of proton dissociable chromogenic crown ether reagents for determination of alkali metal ions have been noticed [1–3]. The introducing of azo chromophore into crown ether ring should emphasised complexing abilities of the crown ether. The described crown ether has two azo groups as a part of macrocycle and phenolic OH group directed inside crown ether cavity.

Novel chromogenic 21-membered crown ether has been synthesized as described previously [4] and used as a complexing reagent for alkali metal cations.



(1) n = 2
(2) n = 1

The absorption spectra of the complexes of crown ether (1) with Li$^+$, Na$^+$, K$^+$ were measured in dioxane-water (1:1 % v/v) system in the presence of triethylamine (TEA). The TEA concentration required to observe color changes during complexation of the crown ether with metal cations was examined. The absorbance remained constant at the final concentration of TEA 3% v/v. Absorption spectra of azocrown ether (Figure 1) showed no absorption band in the region about 500 nm. Addition of lithium chloride to a crown ether solution creates a new absorption band at λ_{max}= 538 nm (Figure 1). The spectra were measured up to high cation to crown ether ratio and the limiting spectra were obtained. A well pronounced isosbestic point for the system containing lithium suggests the presence of two absorbing species at the equilibrium. The formation constants were estimated according to the Benesi – Hildebrandt method [5]. On the base of factor analysis [6] the absorption of crown ether and absorption of totally complexed

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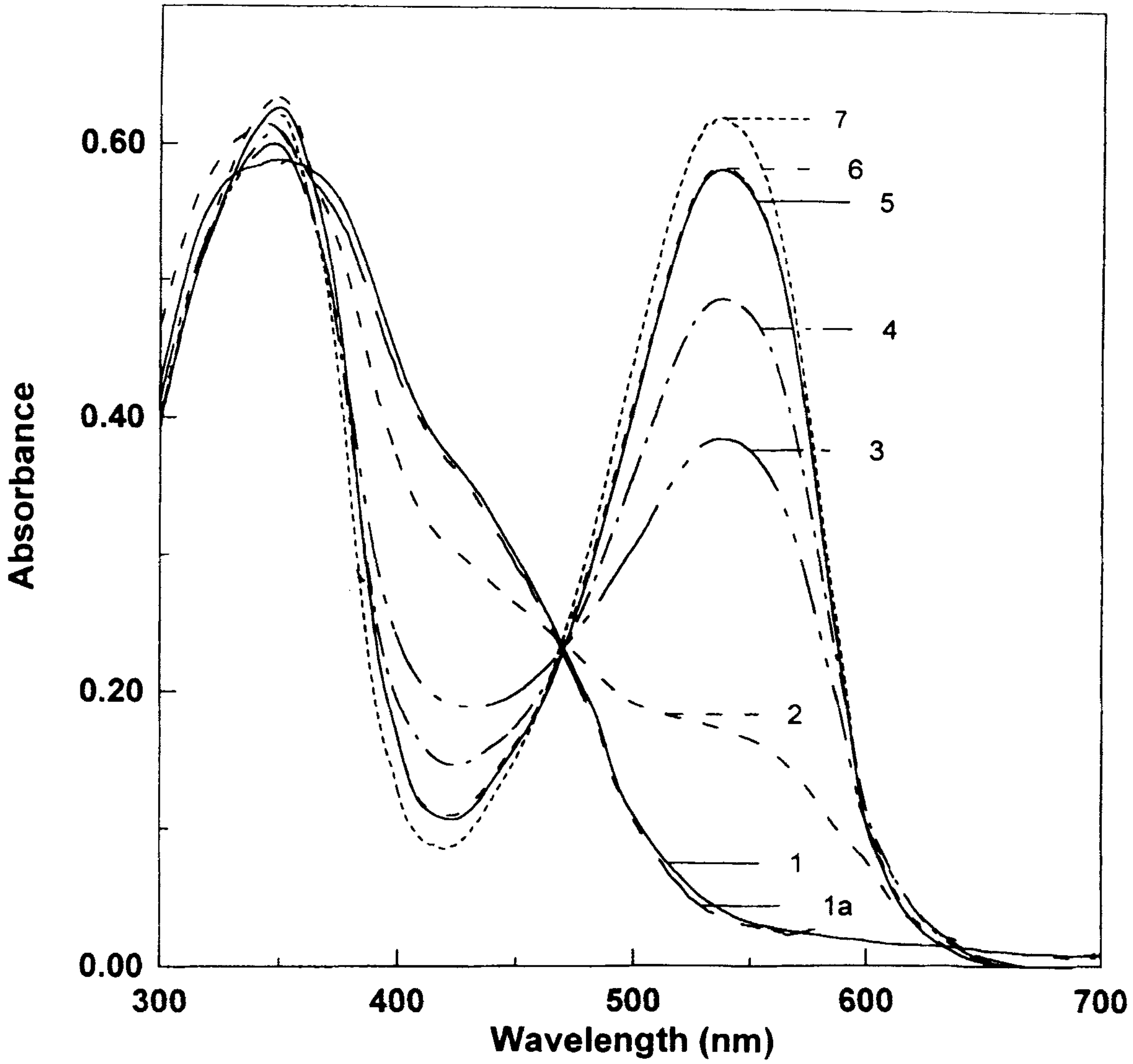

FIGURE 1 Absorption spectra of 21-membered azocrown ether – LiCl system in dioxane – water. Azocrown ether concentration 2.6x10^{-5} M, TEA (3% v/v). (1) salt free, (la) calculated spectra for uncomplexed crown ether, (2) 0.0014; (3) 0.005; (4) 0.01; (5) 0.05; (6) 0.1 M of LiCl; (7) calculated spectra for totally complexed crown ether

crown ether were calculated. The formation constant value for this system is given in Table I.

When sodium or potassium chloride is added to azocrown ether (**1**) solution in dioxane – water -TEA system a new absorption bands appears at λ_{max}=538 nm but absorption changes are smaller than in the presence of lithium chloride (Figure 2). The formation constants for complexes of azocrown ether with these cations are given in Table I. Rubidium or cesium salts added to the solution of azocrown ether (**1**) in dioxane – water – TEA do not cause formation of any new absorption band in the mentioned region.

Addition of strong bases like tetraethylamonium hydroxide or tetrabuthylamonium hydroxide to 21-membered azocrown ether in dioxane –

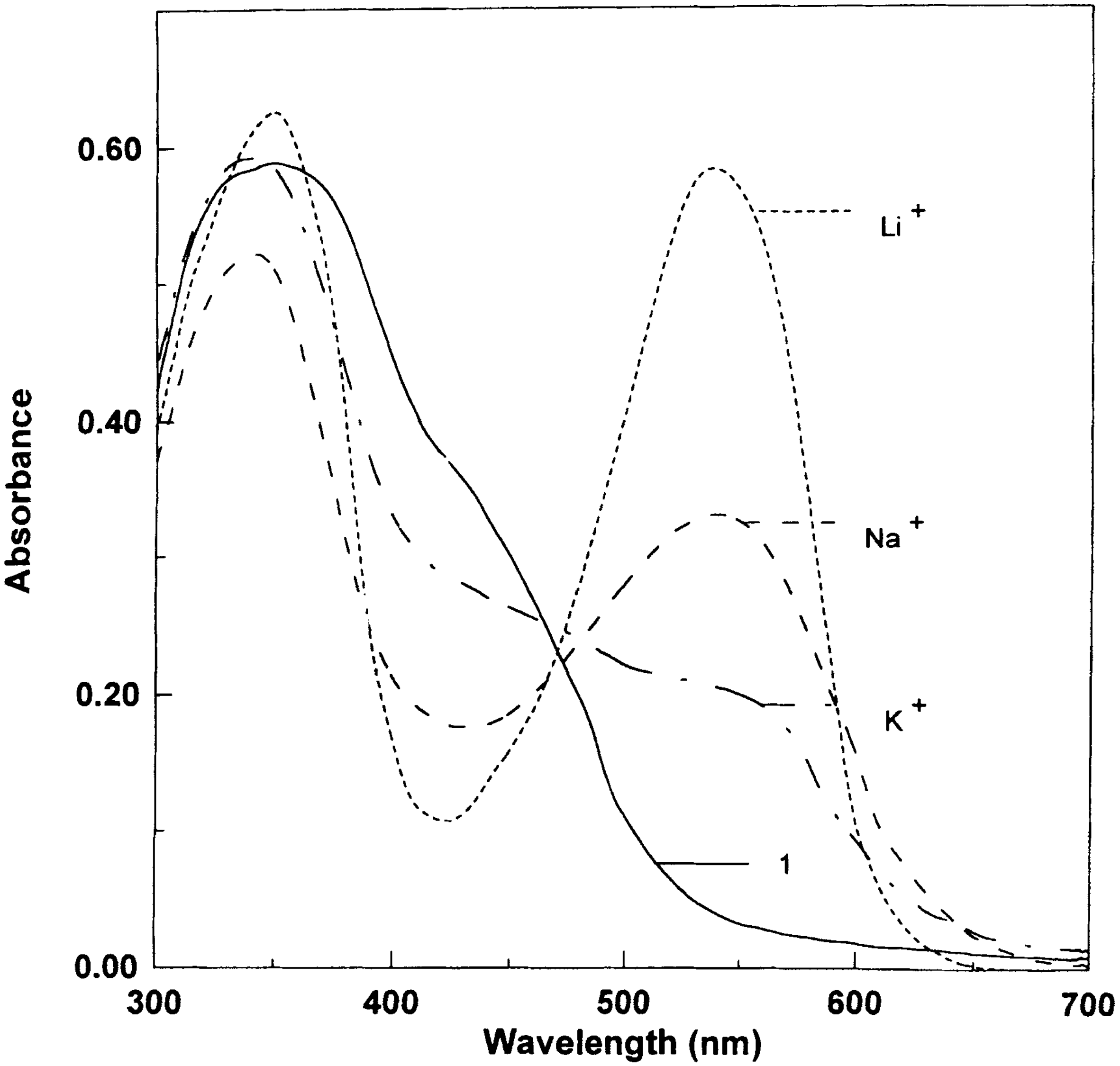

FIGURE 2 Absorption spectra of 21-membered azocrown ether – MCl system in dioxane – water. Azocrown ether concentration 2.6x10^{-5} M, TEA (3% v/v). (1) – salt free, Concentrations of MCl 0.05 M

water solution is also accompanied by formation of a absorption band at λ_{max}=538 nm. This is in contrary to 18-membered azocrown (2) ether where analogous absorption band does not appear when tetraethylamonium hydroxide is added to the solution [4].

Complexing properties are also observed for 18-membered azocrown ether (2) with Li$^+$, Na$^+$, K$^+$ in dioxane – water solution in the presence of TEA although for those systems absorption changes at λ_{max} are much smaller than for analogous solutions of 21-membered azocrown ether (1) and consequently formation constants are much lower. The formation constants for azocrown ether (2) with investigated cations are given in Table I.

TABLE I Complex formation constants in dioxane – water

Salt	*21-membered azocrown ether with*	*18-membered azocrown ether with*	
	TEA *K* (M^{-1})	*TEA* *K* (M^{-1})	$Et_4NOH^{[4]}$ *K* (M^{-1})
LiCl	230	50	880
NaCl	123	14	326
KCl	51	5	82

The investigated 21-membered azocrown ether (**1**) in dioxane solution showed a characteristic color change when lithium salt is added without addition of triethylamine. The color changed dramatically from yellow to pink even in the presence of traces of lithium salts, the new absorption band appeared at λ_{max}=538 nm. The reaction in dioxane solution is characteristic for lithium ion and is not observed for any other alkali metal cation.

The complexing abilities of the novel azocrown ether (**1**) are noticed also with divalent cations. When barium salt is added to the solution of azocrown ether (**1**) in dioxane the new absorption band is observed at longer wavelength (λ_{max}=588 nm) without adding of TEA buffer. To observe spectral changes accompanying complexation of strontium, calcium or nickel cations with azocrown ether (**1**) the presence of triethylamine is required.

CONCLUSIONS

The investigated 21-membered azocrown ether exhibit complexing properties with Li^+, Na^+, K^+ in dioxane-water-TEA solution with the most pronounced absorption changes for lithium. The complexation in pure dioxane of even traces of lithium without buffer is very sensitive quantitative color reaction (the yellow solution turned to pink). The novel 21-membered azocrown ether is better lithium reagent than 18-membered azocrown ether and could be used as an analytical reagent to identify small amount of lithium cations.

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