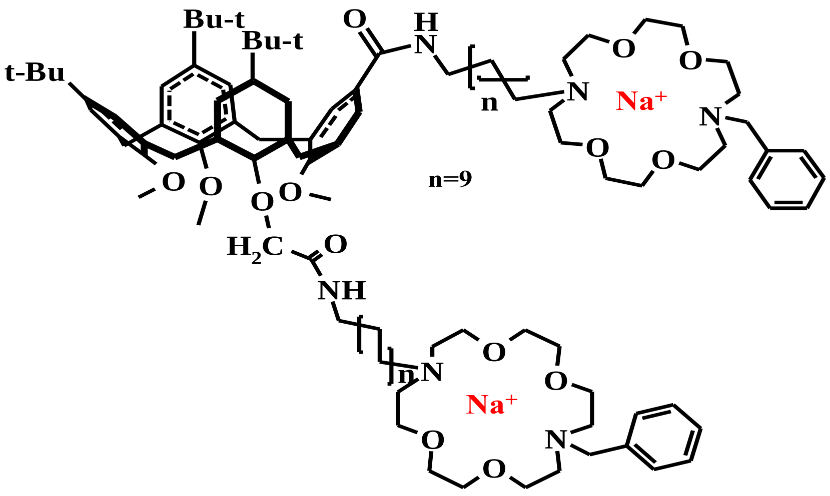
Extraction and complexing abilities of a series of p-tert-butylcalix[4]arenes substituted by N-carbonylmonoaza-12-crown-4

Elena Alekseeva *, Ekaterina Kulygina and Tatiana Kirichenko

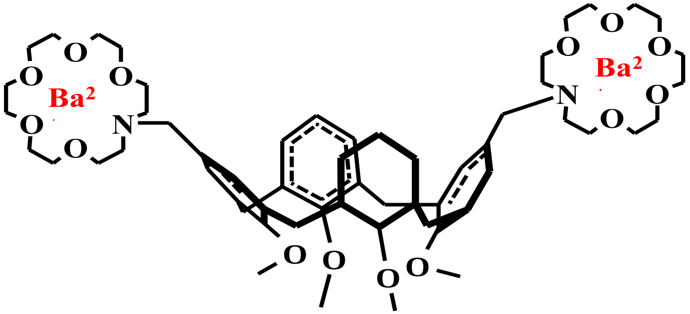
A.V. Bogatsky Physico-Chemical Institute of the National Academy of Sciences of Ukraine,
Lustdorfska doroga, 86, 65080 Odesa, Ukraine; office.physchem@nas.gov.ua
* Correspondence: AlekseevaEA@nas.gov.ua

The present study is a continuation of our work on the complexing properties of supramolecular architectures based on calixarenes and crown ethers. This work discloses the complexing and extraction abilities of calix[4]arene derivatives depending upon the size of the intramolecular cavity formed by different numbers of identical crown ether substituents. The extraction and complexing properties of a series of p-tert-butylcalix[4]arene derivatives containing N-methoxycarbonylmonoaza-12-crown-4 as substituents were evaluated through liquid-liquid extraction and spectrophotometric titration methods. It has been demonstrated that monosubstituted calixarene is an effective and highly selective extractant towards to sodium cations. Calixarene's derivative comprising two crown ether substituents tend to interact with alkali metal cations with formation of 1:1 complexes. On the contrary, cesium cation forms with the disubstituted calixarene a biligand mononuclear complex. The tetrasubstituted analog is an effective but not selective extractant for both s-element cations and cadmium cations in the d-element series. Both tri- and tetrasubstituted calixarenes form mononuclear complexes with sodium cations in the alkali metal series and calcium ions in the alkaline earth metal series with $\lg K>5$. At the same time, these macrocycles form the complexes of 1:1 and 1:2 compositions (ligand-cation) with barium and strontium cations. The ability of calix[4]arene with four crown ether substituents to form binuclear complexes with cations of transition metals - copper, nickel, cobalt and cadmium - has also been demonstrated.

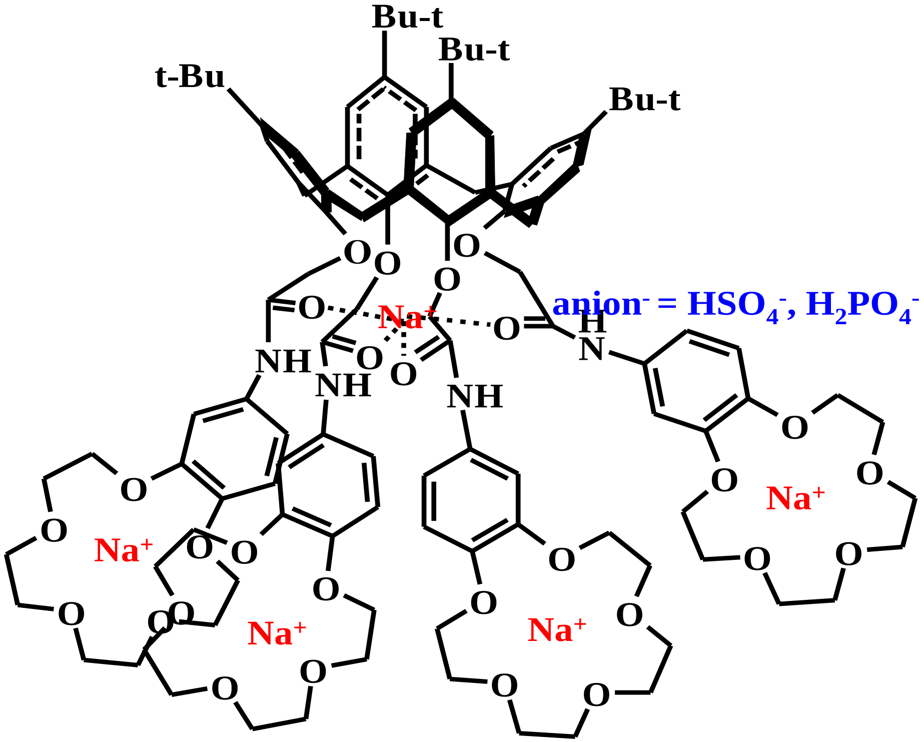
What was before



New.J.Chem. **2008**, *32*, 878–890

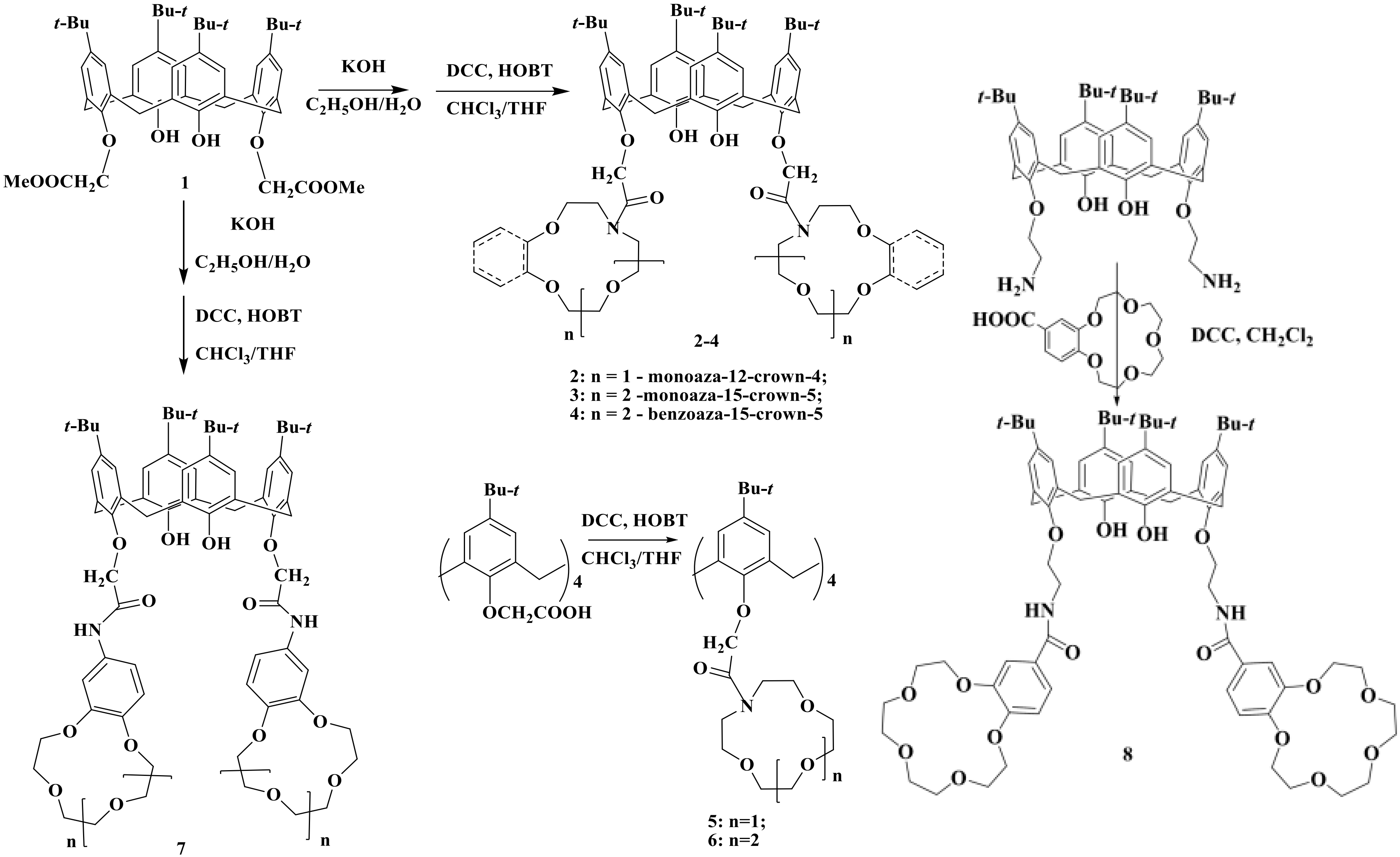


Chem. Eur. J. **2000**, *6*, 1322–1330



J. Chem. Soc., Dalton Trans.
1995, *19*, 3117–3124

What we have done



2: n = 1 - monoaza-12-crown-4;
3: n = 2 -monoaza-15-crown-5;
4: n = 2 - benzoaza-15-crown-5

5: n=1;
6: n=2

7: n = 2 - amidobenzo-15-cron-5

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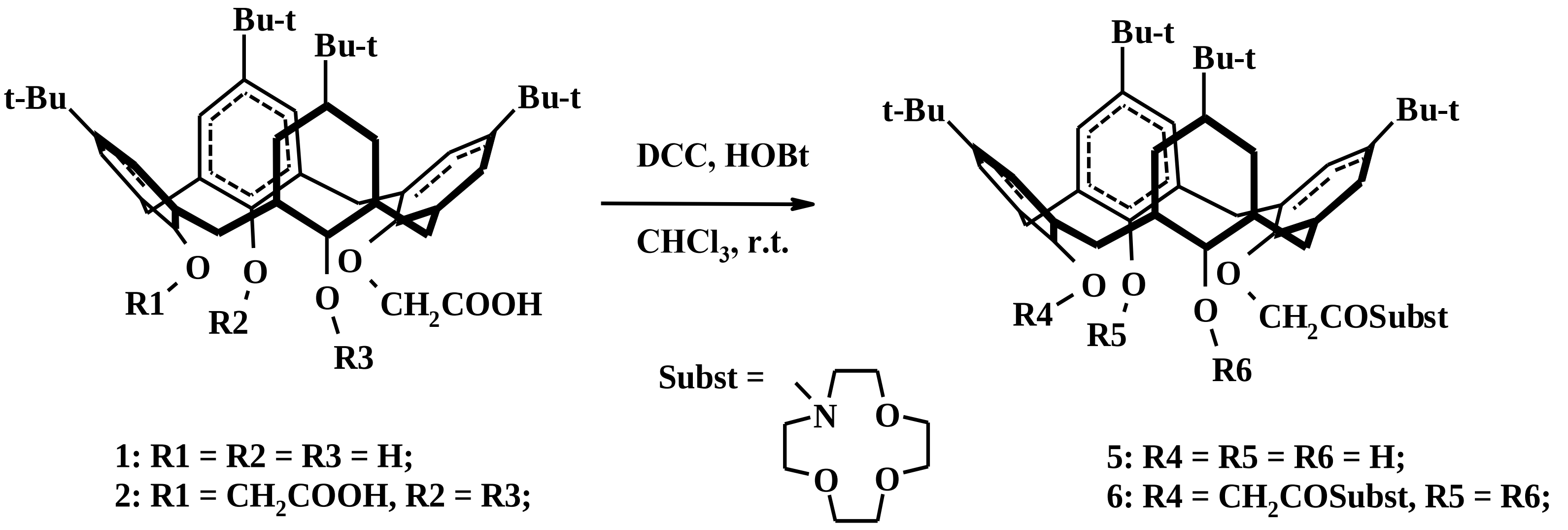
What now?



1: R1 = R2 = R3 = H;
2: R1 = CH$_2$COOH, R2 = R3;
3: R1 = H, R2 = R3 = CH$_2$COOH;
4: R1 = R2 = R3 = CH$_2$COOH

5: R4 = R5 = R6 = H;
6: R4 = CH$_2$COSubst, R5 = R6;
7: R4 = H, R5 = R6 = CH$_2$COSubst;
8: R4 = R5 = R6 = CH$_2$COSubst

In order to evaluate the ability of calix[4]arenes with crown ether substituents to recognize metal ions, a liquid-liquid extraction experiment with alkali, alkaline earth and some transition metal picrates has been carried out.

Extraction (%) of picrates by calixarene derivatives 5-8 at ligand-metal ratio - 1:1. ($CHCl_3$-H_2O, 20ºC, Lig – $2.5x10^{-4}$ M, Met – $2.5x10^{-4}$ M)

Comp.	Li^+	Na^+	K^+	Rb^+	Cs^+	Ca^{2+}	Sr^{2+}	Fe^{3+}	Cu^{2+}	Cd^{2+}
mono-	-*	77.4	15.8	15.91	9.1	-	4.08	26.3	7.16	7.17
di-	-	29.57	24.74	13.41	5.7	3.71	4.1	21.7	7.19	2.0
tri-	-	47.81	11.27	22.8	9.57	7.42	15	58.4	18.86	14.5
tetra-	50.4	94.6	80.25	30.6	46.36	37.39	45.3	54.16	23.7	53.4

* “-“ – no extraction

Note that when studying the extraction properties of all calixarenes toward to magnesium and barium cations a re-extraction process with a partial transition of the resulting complexes into the aqueous phase was observed

Stability constants ($\lg K_n$) of the complexes of calixarenes 5-8 with alkali and alkaline earth metal cations in MeOH

Comp.	**Cation**								
		Li^+	**Na^+**	**K^+**	**Rb^+**	**Cs^+**	**Ca^{2+}**	**Sr^{2+}**	**Ba^{2+}**
mono-	$\lg K_1$	-*	3.69	-	-	-	-	-	-
di-	$\lg K_{11}$	-	2.31	2.98	2.57	2.27	2.62	2.98	3.66
	$\lg K_{21}$					6.67			
tri-	$\lg K_{11}$	-	>7	3.64	3.09	2.15	>7	5.15	5.24
	$\lg K_{12}$		-	2.73	2.57	-	-	2.67	3.27
tetra-	$\lg K_{11}$	1.21	5.57	3.40	-	-	5.59	5.12	4.80
	$\lg K_{12}$	3.46						1.69	2.28

* The changes in spectrum were too small and it was impossible to calculate the binding constant.

The introduction of several aza-12-crown-4 ether residues into the preorganized structure of calix[4]arene in the cone conformation will, in our opinion, make it possible to create a polytopic receptor for transition metal ions.

Stability constants (lgK_n) of the complexes of tetrasubstituted calixarene with cations of some transition metals (ion. rad.) in MeOH

lgK_n	**Cation**					
	Mn^{2+} (1.60)	**Fe^{3+}** (1.28)	**Co^{2+}** (1.48)	**Ni^{2+}** (1.38)	**Cu^{2+}** (1.44)	**Cd^{2+}** (1.94)
lgK_{11}	3.02	2.88	3.24	2.80	4.95	4.81
lgK_{12}			2.54	2.86	2.02	4.12

Thus, a change in the extraction and complexing properties of calix[4]arenes with azacrown ether substituents - potential complexones - has been demonstrated, depending on the number of crown ether substituents included in the calixarene molecule.