EXTRACTION OF ALKALINE AND ALKALINE-EARTH METAL CATIONS AT SYNERGISTIC ACTION OF BIS[UNDECAHYDRO-7,8-DICARBAUNDECA-BORATO(2–)]COBALTATE(1–) AND SUBSTITUTED CALIX[n]ARENES IN NITROBENZENE

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The extraction of alkaline and alkaline-earth metal cations at synergistic action of bis[undecahydro-7,8-dicarbaundecaborato(2–)]cobaltate(1–) and substituted calix[n]arenes ($n = 4$ and 6) in nitrobenzene was investigated. It was found that the lower-rim-substituted calix[4]arene with four (diethylcarbamoyl)methyl groups extracts calcium, strontium and barium in the systems under study much better than calixarenes which do not contain amide groups. Synergistic factor values log $S(Ca) \approx 7$, log $S(Sr) \approx 5.5$ and log $S(Ba) \approx 5.4$ were found. The competition of K^+ and Na^+ in the extraction of strontium is much lower than in analogous systems containing crown ethers. The addition of calixarene causes a synergistic effect in the extraction of sodium and an antagonistic effect in the extraction of cesium.
Key words: Calixarenes; Water–nitrobenzene extraction system; Bis[undecahydro-7,8-dicarbaundecaborato(2–)]cobaltate(1–); Dicarbollide; Carboranes; Calcium; Strontium; Barium.

Both cyclic and acyclic polyoxonium compounds[1–4] have been used to facilitate extraction and transport of ions across the boundary of two immiscible phases. Recently, also calix[n]arenes have been frequently used for this purpose[1,5–9]. These compounds are extremely versatile due to well-developed synthetic derivatization procedures for both rims of the calix[n]arene skeleton. An extraction system of particular interest is based on solution of polyoxonium compounds in combination with big hydrophobic anions in polar media such as nitrobenzene. It was found that high separation factors for alkaline and alkaline-earth metal cations can be achieved using this system[10,11]. The aim of this work is to study alkaline and alkaline-earth metal cation extraction using a system with substituted calix[n]arene–cobalt(III)dicarbollide in water, mineral acid and nitrobenzene. Calix[n]arenes, denoted as **1–5** were chosen for this study.

EXPERIMENTAL

Calix[4]arenes **1**–**5** are relatively easily accessible from parent calix[*n*]arenes by alkylation of lower-rim phenolic hydroxy groups. Thus 5,11,17,23,29,35-hexa-*tert*-butyl-37,38,39,40,41,42-hexakis(1,4,7,10-undecanyl)calix[6]arene (**1**) was prepared by alkylation of hexaanion of calix[6]arene with 3,6,9-trioxa-decyl-4-methylbenzenesulfonate in DMF at 60 °C according to known procedure[12]. Analogously, 5,11,17,23-tetra-*tert*-butyl-25,27-bis(1,4,7-trioxanonyl)-2,14-dihydroxycalix[4]arene (**2**) was prepared in 54% yield by slightly modified procedure published for 5,11,17,23-tetra-*tert*-butyl-25,27-bis(1,4-dioxahexyl)-26,28-dihydroxycalix[4]arene (**3**) (ref.[13]) (see below). Later, 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrakis(ethoxycarbonylmethyleneoxy)calix[4]arene (**4**) and 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrakis(*N*,*N*-diethylcarboxamidomethyleneoxy)calix[4]arene (**5**) were prepared according to published procedures[14].
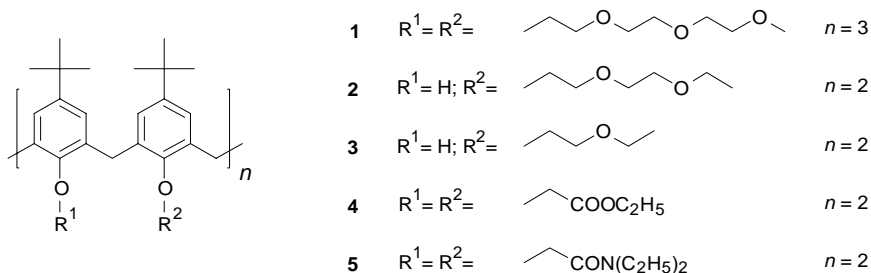
5,11,17,23-Tetra-*tert*-butyl-2,14-bis(1,4,7-trioxanonyl)calix[4]arene (**2**)

5,11,17,23-Tetra-*tert*-butylcalix[4]arene (1.0 g, 2.36 mmol) and 3,6-dioxaoctyl bromide (0.91 g, 4.95 mmol) were dissolved in 20 ml dry acetonitrile and stirred with dry potassium carbonate (0.49 g) under reflux for 3 h. The reaction mixture was then cooled, filtered, solids were repeatedly washed with cold acetonitrile and filtrate was concentrated in vacuum and partitioned between water and chloroform (100 + 100 ml). The organic phase was separated and the aqueous phase was extracted with chloroform; the organic phases were combined, dried with magnesium sulfate, filtered, evaporated in vacuum and the crude product was crystallized from chloroform–methanol giving 0.85 g (55%) of **2** in form of white crystals, m.p. 194–195 °C. For $C_{56}H_{80}O_8$ (881.24) calculated: 76.30% C, 9.20% H; found: 76.80% C, 8.96% H.

Cesium bis[undecahydro-7,8-dicarbaundecaborato(2–)cobaltate(1–) synthesized in Institute of Inorganic Chemistry, Academy of Sciences of the Czech Republic was transferred to acid form (cobalt(III)dicarbollide, H^+B^-) using a standard procedure[15]. Its concentration was assayed using two-phase potentiometric titration using carbonate-free sodium hydroxide (RTS 822, Radiometer, Copenhagen, Denmark). Other chemicals were from Lachema (Czech Republic) of analytical reagent purity. Radionuclides [45]Ca (DuPont, Belgium), [85]Sr (DuPont, Belgium), [134]Cs (Techsnaveksport, Russia), [22]Na (DuPont, Belgium) and [133]Ba (Polatom, Poland) were used as obtained and of standard radiochemical purity.

Extractions were performed by shaking equal amounts (1 ml) of both phases in rotating extractor overnight at 25 ± 2 °C. The initial concentration of extracted metal ions in the aqueous phase was $1 \cdot 10^{-6}$ mol/l. After that time equilibrium was attained. Both phases were separated by centrifugation (5 min, 40 s^{-1}). For radioactivity measurements 0.5 ml samples of both phases were withdrawn and distribution ratios (*D*) of Na$^+$, Cs$^+$, Ba^{2+} and Sr^{2+} were determined by γ-ray measurement using a

well-type NaI(Tl) scintillation detector in conjunction with one-channel analyzer RFT Strahlungs-messgerät 20046 (RFT, Dresden, Germany). The distribution ratios of Ca were determined radiometrically by measuring β-activities of dried samples using a scintillation plastic detector in conjunction with the above analyzer.

RESULTS AND DISCUSSION

The results of extraction of Sr with cobalt(III)dicarbollide and calixarenes **1**–**5** in nitrobenzene are summarized in Table I. The mentioned initial concentrations $c(HNO_3)$, $c(H^+B^-)$ and $c(L)$ are always related to the volume of single phase. It is evident that disubstituted calixarenes **2** and **3** have no promoting effect on extraction. Hexasubstituted calix[6]arene **1** promotes extraction to a very similar extent like crown ethers based on 18-crown-6 (ref.[16]). Calixarene tetraester **4** promotes extraction increasing the distribution ratio of strontium by factor $S \approx 4$. This effect, however, can be considered negligible in comparison with tetramide **5**. This compound has a remarkable effect on extraction showing the synergistic factor $S \approx 300\,000$ which is comparable with those of 15-crown-5 and benzo-15-crown-5 (ref.[16]). Synergistic coefficients are calculated as a ratio of the distribution ratio of the metal ion in the system under study and the distribution ratio measured in the same concentrations of nitric acid and cobalt(III)dicarbollide in the absence of calixarene. It differs from the usual definition $S = D_{1,2}/(D_1 + D_2)$. The distribution ratios of Ca, Sr and Ba found for the extraction by the nitrobenzene solutions of compound **5** in the absence of cobalt(III)dicarbollylcobaltate are always much lower than that of the cobalt(III)dicarbollide–calixarene mixture.

The effect of competing ion concentration is shown in Table II for compounds **1** and **5**. It is clear that Ca^{2+} in concentration 0.05 mol/l suppresses extraction of strontium in systems with **1** and even more with **5**. Extraction of Sr^{2+} is influenced by Ca^{2+} concen-

TABLE I
Extraction of strontium with nitrobenzene solutions of cobalt(III)dicarbollide in the presence of substituted calix[n]arenes (n = 4, 6)[a]

Calixarene	$c(H^+B^-)$, mol/l	$c(L)$, mol/l	$D(Sr)$	S
1	0.01	0.005	3.9	130
2	0.01	0.005	0.023	0.73
3	0.00855	0.00428	0.020	0.87
4	0.01	0.005	0.134	4.36
5	0.01	0.0047	10 000	300 000
5	0.004	0.00188	4 800	600 000

[a] $c(HNO_3)$ = 0.1 mol/l.

tration to a higher extent than in systems with 15-crown-5 derivatives, the effect of ions Na$^+$ and K$^+$ on the other hand, being much smaller[16,17]. It is necessary to stress the high selectivity Sr^{2+}/K$^+$ which seems very important provided it is usually potassium which is frequently competing with extraction of strontium using common polyoxonium compounds. Calixarene **5** is 30 times and 200 times less sensitive to sodium and potassium cations, respectively, when compared with extractions using 15-crown-5 derivatives.

Further studies were carried out in systems with calixarene **5**. The concentrations of **5** influences the extraction of Ca^{2+}, Sr^{2+}, Ba^{2+} ions as shown in Fig. 1. Typical maxima in the dependences of the distribution ratios, D, on the analytical concentration of calixarene, $c(L)$ (known from studies with poly(ethylene glycol)s, polyethers and crown compounds[10,15–19]) can be clearly seen. This can be explained in terms of competition among extracted ions and H$^+$ ions, which protonizes calixarene in nitrobenzene. The values of maximal synergistic factors are: log S(Ca) ≈ 7, log S(Sr) ≈ 5.5 and log S(Ba) ≈ 5.4

TABLE II
The influence of concentration of competitive ions on extraction of strontium with nitrobenzene solutions of cobalt(III)dicarbollide in the presence of calixarenes **5** and **1**^{a}

Calixarene	Competitive ion, M	$c(M)$, mol/l	$c(L)$, mol/l	$D(Sr^{2+})$
1	–	–	0.005	3.9
1	Ca^{2+}	0.05	0.005	0.11
5	–	–	0.0047	10 000
5	Ca^{2+}	0.05	0.0047	0.021
5	K$^+$	0.02	0.0047	3 500
5	Na$^+$	0.02	0.0047	680

^{a} $c(HNO_3) = 0.1$ mol/l, $c(H^+B^-) = 0.01$ mol/l.
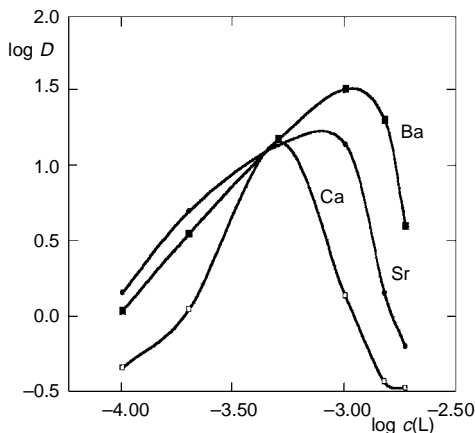

FIG. 1
log D(Ca), D(Sr) and D(Ba) as a function of log $c(L)$ in the water–HNO$_3$–metal ion (microamounts)–nitrobenzene–cobalt(III)dicarbollide–calixarene **5** system. $c(H^+B^-) = 0.001$ mol/l. $c(HNO_3)$, mol/l: Ca 1.0; Sr 0.1; Ba 0.1

(for comparison, extraction using PEG 400 has shown the following values[18]: $\log S(Ca) \approx 2.5$, $\log S(Sr) \approx 4.5$ and $\log S(Ba) \approx 6.5$, and using 15-crown-5 (ref.[17]): $\log S(Ca) \approx 3.5$, $\log S(Sr) \approx 6$ and $\log S(Ba) > 7$). Until recently the extraction of Ca^{2+} was believed to be most selective done in the system 12-crown-4–water–HNO_3–cobalt(III)dicarbollide–nitrobenzene[18,19]. However, the latter system is still 1 000 times less efficient when compared with system using calixarene **5** shown here. The extraction can be performed with $1 \cdot 10^{-3}$ M cobalt(III)dicarbollide in nitrobenzene and 1 M HNO_3.

Table III shows the dependence of the distribution ratio of cesium ion on concentration of **5**. The higher the concentration of **5** the lower the extraction, probably as a result of protonation of **5** in organic phase. The protonated calixarene **5** competes not only with cesium complexation but also with the transfer of Cs^+ cation to organic phase. Extraction of sodium cation (Table IV), on the contrary, is enhanced with increasing concentration of **5**. This can be easily explained by the fact that the stability of calixarenes complex $5 \cdot Na^+$ is much higher than that of complex $5 \cdot H^+$.

TABLE III
Extraction of cesium with nitrobenzene solution of cobalt(III)dicarbollide in the presence of calixarene **5**[a]

$\log c(L)$	$\log D(Cs^+)$
–	1.089
–3.328	0.619
–2.726	–2.741

[a] $c(HNO_3) = 0.1$ mol/l, $c(H^+B^-) = 0.001$ mol/l.

TABLE IV
Extraction of sodium with nitrobenzene solution of cobalt(III)dicarbollide in the presence of calixarenes **4** and **5**[a]

Calixarene	$c(H^+B^-)$	$c(L)$	D	$\log D$
–	0.01	0	0.0635	–1.20
4	0.01	0.0050	0.225	–0.65
5	0.01	0.0047	1.513	0.18
5	0	0.0047	0.757	–0.121

[a] $c(HNO_3) = 0.1$ mol/l, $c(H^+B^-) = 0.01$ mol/l.

REFERENCES

1. Gokel G. W. (Ed.): *Molecular Recognition, Receptors for Cationic Guests, Comprehensive Supramolecular Chemistry*. Vol. 1. Pergamon, London 1996.
2. Gokel G. W. in: *Crown Ether and Cryptands* (J. F. Stoddart, Ed.). RSC, Cambridge 1991.
3. Hiraoka M.: *Crown Compounds, Their Characteristics and Applications*. Kodansha, Tokyo 1982.
4. Dobler M.: *Ionophores and Their Structures*. Wiley, New York 1981.
5. Gutsche C. D. in: *Calixarenes* (J. F. Stoddart, Ed.), Vol. 1. RSC, Cambridge 1989.
6. Bohmer V.: *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 713.
7. Diamond D., McKervey M. A.: *Chem. Soc. Rev.* **1996**, 15.
8. Ludwig R.: *Review on Calixarene-type Macrocycles and Metal Extraction Data*, Rep. JAERI-Review-95-022. JAERI, Tokyo 1995.
9. Dozol J. F., Bohmer V., McKervey M. A., Lopez Calahora F., Reinhoudt D. N., Schwing M.-J., Ungaro R., Wipf G.: Rep. EUR 17615 EN. European Communities, Luxembourg 1997.
10. Makrlik E., Vanura P.: *Talanta* **1985**, *32*, 423.
11. Kyrs M.: *Radioanal. Nucl. Chem.* **1994**, *187*, 185.
12. Nomura E., Taniguchi H., Kawaguchi K., Otsuji Y.: *J. Org. Chem.* **1993**, *58*, 4709.
13. Verboom W., Datta S., Asfari Z., Harkema S., Reihoudt D. N.: *J. Org. Chem.* **1992**, *57*, 5394.
14. Collins E. M., McKervey M. A., Madigan E., Moran M. B., Owens M., Ferguson G., Harris S. J.: *J. Chem. Soc., Perkin Trans. 1* **1991**, 3137.
15. Vanura P., Makrlik E.: *Collect. Czech. Chem. Commun.* **1985**, *50*, 581.
16. Vanura P., Jedinakova-Krizova V., Valentova Z.: *J. Radioanal. Nucl. Chem.* **1996**, *208*, 283.
17. Vanura P.: *J. Radioanal. Nucl. Chem.* **1998**, *228*, 43.
18. Vanura P., Makrlik E., Rais J., Kyrs M.: *Collect. Czech. Chem. Commun.* **1982**, *47*, 1444.
19. Vanura P.: *13th Radiochemical Conference, Marianske Lazne, 19.–24.4.1998*, Czech Republic, Abstr. No. P6-28. Czech Chemical Society, Marianske Lazne 1998.