

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/270969217>

# Calix[4]arene-bis(coumarin-crown-6) as an extraordinarily effective macrocyclic receptor for Cs<sup>+</sup>, Ag<sup>+</sup>, and Tl<sup>+</sup>

ARTICLE in JOURNAL OF INCLUSION PHENOMENA AND MACROCYCLIC CHEMISTRY · FEBRUARY 2015

Impact Factor: 1.43 · DOI: 10.1007/s10847-014-0446-y

---

READS

16

## 4 AUTHORS, INCLUDING:



E. Makrlík

371 PUBLICATIONS 4,148 CITATIONS

SEE PROFILE



Petr Vaňura

University of Chemistry and Technology, Pr...

357 PUBLICATIONS 3,514 CITATIONS

SEE PROFILE



Pavel Selucký

ÚJV Řež, a. s.

153 PUBLICATIONS 1,913 CITATIONS

SEE PROFILE

# Calix[4]arene-bis(coumarin-crown-6) as an extraordinarily effective macrocyclic receptor for $\text{Cs}^+$ , $\text{Ag}^+$ , and $\text{Tl}^+$

Emanuel Makrlík · Petr Vaňura · Pavel Selucký ·  
Zouhair Asfari

Received: 13 February 2014 / Accepted: 27 August 2014 / Published online: 9 October 2014  
© Springer Science+Business Media Dordrecht 2014

**Abstract** On the basis of extraction experiments and  $\gamma$ -activity measurements, the exchange extraction constants corresponding to the general equilibrium  $\text{M}^+(\text{aq}) + \mathbf{1} \cdot \text{Cs}^+(\text{nb}) \rightleftharpoons \mathbf{1} \cdot \text{M}^+(\text{nb}) + \text{Cs}^+(\text{aq})$  occurring in the two-phase water–nitrobenzene system ( $\text{M}^+ = \text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Ag}^+$ ,  $\text{Tl}^+$ ;  $\mathbf{1}$  = calix[4]arene-bis(coumarin-crown-6); aq = aqueous phase, nb = nitrobenzene phase) were evaluated. Moreover, the stability constants of the proved  $\mathbf{1} \cdot \text{M}^+$  complexes in water-saturated nitrobenzene were calculated; they were found to increase in the sequence of  $\text{NH}_4^+ < \text{K}^+ < \text{Rb}^+ < \text{Cs}^+ < \text{Ag}^+ < \text{Tl}^+$ .

**Keywords** Univalent cations · Substituted calix[4]arene compound · Complexation · Extraction and stability constants · Water–nitrobenzene system

## Introduction

Calixarenes are macrocyclic compounds which are not only easily available on a large scale, but also offer nearly boundless possibilities for chemical modification [1]. This makes them highly attractive as the building blocks for more sophisticated and elaborate host molecules. Among the numerous “tailor made” ligands for a large variety of metal cations, crown ether derivatives of calixarenes (calixcrowns) represent not only some of the earliest complexes [2], but also elegantly demonstrate the potential of these compounds [3, 4]. Calixarenes find applications as selective binders and carriers, as analytical sensors, as catalysts and model structures for biomimetic studies [5].

New cesium selective extractants especially from the calix[4]arene-crown-6 and calix[4]arene-bis(crown-6) families have been introduced [6–12]. The corresponding crystal structures of model complexes with cesium salts have demonstrated a significant  $\pi$ -interaction between the facing aromatic rings and the  $\text{Cs}^+$  guest cation, which is also coordinated by the six ether oxygen atoms of the polyether chain [6–8]. Besides, the calix[4]arene-crown-6 family of the mentioned compounds gives  $\text{Cs}^+/\text{Na}^+$  separation factors exceeding  $10^4$  [7].

The dicarbollylcobaltate anion ( $\text{DCC}^-$ ) [13] and some of its halogen derivatives have been applied very often for the solvent extraction of various metal cations (e.g.,  $\text{Cs}^+$ ,  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Eu}^{3+}$ , and  $\text{Am}^{3+}$ ) from aqueous solutions into a polar organic phase, both under laboratory conditions for theoretical or analytical purposes [14–18], and on the technological scale for the separation of some high-activity isotopes in the reprocessing of spent nuclear fuel and acidic radioactive waste [19–21].

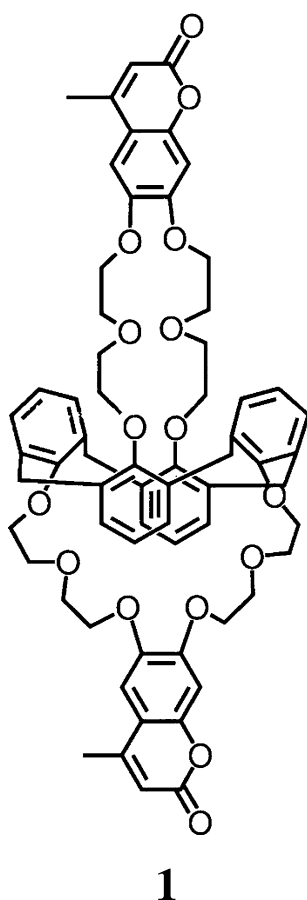
The photophysics of calix[4]arene-bis(coumarin-crown-6) (abbrev. **1**; see Scheme 1) has been reported by Leray

E. Makrlík (✉)  
Faculty of Environmental Sciences, Czech University of Life  
Sciences, Prague, Prague, Kamýcká 129, 165 21 Prague 6, Czech  
Republic  
e-mail: makrlík@centrum.cz

P. Vaňura  
Department of Analytical Chemistry, Institute of Chemical  
Technology, Prague, Technická 5, 166 28 Prague 6, Czech  
Republic  
e-mail: petr.vanura@vscht.cz

P. Selucký  
NRI, 250 68 Řež, Czech Republic  
e-mail: sel@ujv.cz

Z. Asfari  
Institut Pluridisciplinaire Hubert Curien, Laboratoire de Chimie  
Analytique et Sciences Séparatives, UMR 7178 IPHC-DSA,  
ECPM, 25 Rue Becquerel, 67087 Strasbourg Cedex, France  
e-mail: zouhair.asfari@unistra.fr

**1**

**Scheme 1** Structural formula of calix[4]arene-bis(coumarin-crown-6) (abbrev. **1**)

et al. [22]. On the other hand, in the current work, the solvent extraction of  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Ag}^+$ , and  $\text{Tl}^+$  into nitrobenzene by means of a synergistic mixture of cesium dicarbollylcobaltate (CsDCC) [13] and the mentioned receptor **1** was studied. Further, the stability constants of the proved univalent cationic complexes with this substituted calix[4]arene electroneutral ligand **1** were determined in the organic phase of the water–nitrobenzene extraction system. Finally, the stability constants of the considered  $\mathbf{1} \cdot \text{M}^+$  complexes involving the very “hard” and the very “soft” cations were compared and discussed.

## Experimental

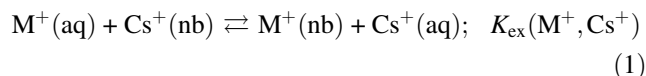
Preparation of compound **1** was described in Ref. [23]. Cesium dicarbollylcobaltate, CsDCC, was synthesized by the method published by Hawthorne et al. [24]. The other chemicals used (Lachema, Brno, Czech Republic) were of reagent grade purity. The radionuclide  $^{137}\text{Cs}^+$  was supplied by Techsnaveksport, Russia; its radionuclidic purity was 99.9 %.

The extraction experiments were carried out in 10 mL polypropylene test-tubes with polypropylene stoppers: 2 mL of an aqueous solution of  $\text{MNO}_3$  ( $\text{M}^+=\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Ag}^+$ ,  $\text{Tl}^+$ ) of the concentration in the range from  $1 \times 10^{-3}$  to  $3 \times 10^{-3}$  M and microamounts of  $^{137}\text{Cs}^+$  were added to 2 mL of a nitrobenzene solution of **1** and CsDCC, whose initial concentrations varied also from  $1 \times 10^{-3}$  to  $3 \times 10^{-3}$  M (in all experiments, the initial concentration of **1** in nitrobenzene,  $C_1^{\text{in,nb}}$ , was always equal to the initial concentration of CsDCC in this medium,  $C_{\text{CsDCC}}^{\text{in,nb}}$ ). The test-tubes filled with the solutions were shaken for 2 h at  $25 \pm 1$  °C, using a laboratory shaker. Then the phases were separated by centrifugation. Finally, 1 mL samples were taken from each phase and their  $\gamma$ -activities were measured by means of a well-type NaI(Tl) scintillation detector connected to a  $\gamma$ -analyzer Triathler (Hidex, Turku, Finland).

The equilibrium distribution ratios of cesium,  $D_{\text{Cs}}$ , were determined as the ratios of the corresponding measured radioactivities of  $^{137}\text{Cs}^+$  in the nitrobenzene and aqueous samples.

## Results and discussion

Regarding the results of previous papers [13, 25, 26], the two-phase water–  $\text{MNO}_3$  ( $\text{M}^+=\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Ag}^+$ ,  $\text{Tl}^+$ )–nitrobenzene–cesium dicarbollylcobaltate (CsDCC) extraction system can be described by the following equilibrium



with the corresponding exchange extraction constant  $K_{\text{ex}}$  ( $\text{M}^+$ ,  $\text{Cs}^+$ ); aq and nb denote the presence of the species in the aqueous and nitrobenzene phases, respectively. For the constant  $K_{\text{ex}}$  ( $\text{M}^+$ ,  $\text{Cs}^+$ ) one can write [13, 25, 26]

$$\log K_{\text{ex}}(\text{M}^+, \text{Cs}^+) = \log K_{\text{M}^+}^i - \log K_{\text{Cs}^+}^i \quad (2)$$

where  $K_{\text{M}^+}^i$  and  $K_{\text{Cs}^+}^i$  are the individual extraction constants for  $\text{M}^+$  and  $\text{Cs}^+$ , respectively, in the water–nitrobenzene system [25, 26]. Knowing the values of  $\log K_{\text{M}^+}^i$  ( $\text{M}^+=\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ ,  $\text{Ag}^+$ ,  $\text{Tl}^+$ ) [25, 26], the single exchange extraction constants  $K_{\text{ex}}$  ( $\text{M}^+$ ,  $\text{Cs}^+$ ) were simply calculated from Eq. 2. The corresponding data (together with further constants) are given in Table 6.

From previous results [27–29] it follows that the two-phase water–  $\text{MNO}_3$  ( $\text{M}^+=\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Ag}^+$ ,  $\text{Tl}^+$ ) – nitrobenzene–**1**–CsDCC extraction system (see “Experimental” Section), chosen for determination of the stability constant of the  $\mathbf{1} \cdot \text{M}^+$  complex in nitrobenzene saturated

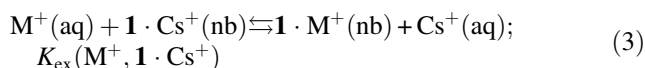
**Table 1** Experimental data concerning determination of  $\log K_{\text{ex}}$  ( $\text{NH}_4^+$ ,  $\mathbf{1}\cdot\text{Cs}^+$ ) on the basis of Eq. (5) for  $\text{M}^+=\text{NH}_4^+$ 

$\text{C}_{\text{NH}_4\text{NO}_3}^{\text{in, aq}}$ (M)	$\text{C}_{\text{CsDCC}}^{\text{in, nb}}$ (M)	$D_{\text{Cs}}$	$\log K_{\text{ex}} (\text{NH}_4^+, \mathbf{1}\cdot\text{Cs}^+)$
$1.0 \times 10^{-3}$	$1.0 \times 10^{-3}$	135.8	−4.3
$1.5 \times 10^{-3}$	$1.5 \times 10^{-3}$	136.2	−4.3
$2.0 \times 10^{-3}$	$2.0 \times 10^{-3}$	122.3	−4.2
$2.5 \times 10^{-3}$	$2.5 \times 10^{-3}$	138.4	−4.3
$3.0 \times 10^{-3}$	$3.0 \times 10^{-3}$	150.5	−4.4

**Table 2** Experimental data concerning determination of  $\log K_{\text{ex}}$  ( $\text{K}^+$ ,  $\mathbf{1}\cdot\text{Cs}^+$ ) on the basis of Eq. (5) for  $\text{M}^+=\text{K}^+$ 

$\text{C}_{\text{KNO}_3}^{\text{in, aq}}$ (M)	$\text{C}_{\text{CsDCC}}^{\text{in, nb}}$ (M)	$D_{\text{Cs}}$	$\log K_{\text{ex}} (\text{K}^+, \mathbf{1}\cdot\text{Cs}^+)$
$1.0 \times 10^{-3}$	$1.0 \times 10^{-3}$	7.35	−1.7
$1.5 \times 10^{-3}$	$1.5 \times 10^{-3}$	7.82	−1.8
$2.0 \times 10^{-3}$	$2.0 \times 10^{-3}$	7.44	−1.7
$2.5 \times 10^{-3}$	$2.5 \times 10^{-3}$	8.01	−1.8
$3.0 \times 10^{-3}$	$3.0 \times 10^{-3}$	8.55	−1.9

with water, can be characterized by the main chemical equilibrium (3):



with the general equilibrium extraction constant  $K_{\text{ex}}$  ( $\text{M}^+$ ,  $\mathbf{1}\cdot\text{Cs}^+$ ):

$$K_{\text{ex}}(\text{M}^+, \mathbf{1} \cdot \text{Cs}^+) = \frac{[\mathbf{1} \cdot \text{M}^+]_{\text{nb}} [\text{Cs}^+]_{\text{aq}}}{[\text{M}^+]_{\text{aq}} [\mathbf{1} \cdot \text{Cs}^+]_{\text{nb}}} \quad (4)$$

At this point it is necessary to emphasize that  $\mathbf{1}$  is a considerably lipophilic ligand, practically present in the nitrobenzene phase only, where this ligand forms the very stable complexes  $\mathbf{1}\cdot\text{M}^+$  and  $\mathbf{1}\cdot\text{Cs}^+$ , as given below.

Employing the conditions of electroneutrality in the organic and aqueous phases of the system under study, the mass balances of the univalent cations studied at equal volumes of the nitrobenzene and aqueous phases, as well as the measured equilibrium distribution ratio of cesium,  $D_{\text{Cs}} = [\mathbf{1}\cdot\text{Cs}^+]_{\text{nb}}/[\text{Cs}^+]_{\text{aq}}$ , combined with Eq. 4, we gain the final expression for  $K_{\text{ex}}$  ( $\text{M}^+$ ,  $\mathbf{1}\cdot\text{Cs}^+$ ) in the form

$$K_{\text{ex}}(\text{M}^+, \mathbf{1} \cdot \text{Cs}^+) = \frac{1}{D_{\text{Cs}}} \frac{\text{C}_{\text{CsDCC}}^{\text{in, nb}}}{(1 + D_{\text{Cs}}) \text{C}_{\text{MNO}_3}^{\text{in, aq}} - \text{C}_{\text{CsDCC}}^{\text{in, nb}}} \quad (5)$$

where  $\text{C}_{\text{MNO}_3}^{\text{in, aq}}$  is the initial concentration of  $\text{MNO}_3$  ( $\text{M}^+ = \text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Ag}^+$ ,  $\text{TI}^+$ ) in the aqueous phase and  $\text{C}_{\text{CsDCC}}^{\text{in, nb}}$  denotes the initial concentration of CsDCC in the organic phase of the system under consideration.

**Table 3** Experimental data concerning determination of  $\log K_{\text{ex}}$  ( $\text{Rb}^+$ ,  $\mathbf{1}\cdot\text{Cs}^+$ ) on the basis of Eq. (5) for  $\text{M}^+=\text{Rb}^+$ 

$\text{C}_{\text{RbNO}_3}^{\text{in, aq}}$ (M)	$\text{C}_{\text{CsDCC}}^{\text{in, nb}}$ (M)	$D_{\text{Cs}}$	$\log K_{\text{ex}} (\text{Rb}^+, \mathbf{1}\cdot\text{Cs}^+)$
$1.0 \times 10^{-3}$	$1.0 \times 10^{-3}$	2.39	−0.8
$1.5 \times 10^{-3}$	$1.5 \times 10^{-3}$	2.30	−0.7
$2.0 \times 10^{-3}$	$2.0 \times 10^{-3}$	2.44	−0.8
$2.5 \times 10^{-3}$	$2.5 \times 10^{-3}$	2.53	−0.8
$3.0 \times 10^{-3}$	$3.0 \times 10^{-3}$	2.68	−0.9

**Table 4** Experimental data concerning determination of  $\log K_{\text{ex}}$  ( $\text{Ag}^+$ ,  $\mathbf{1}\cdot\text{Cs}^+$ ) on the basis of Eq. (5) for  $\text{M}^+=\text{Ag}^+$ 

$\text{C}_{\text{AgNO}_3}^{\text{in, aq}}$ (M)	$\text{C}_{\text{CsDCC}}^{\text{in, nb}}$ (M)	$D_{\text{Cs}}$	$\log K_{\text{ex}} (\text{Ag}^+, \mathbf{1}\cdot\text{Cs}^+)$
$1.0 \times 10^{-3}$	$1.0 \times 10^{-3}$	4.70	−1.3
$1.5 \times 10^{-3}$	$1.5 \times 10^{-3}$	5.16	−1.4
$2.0 \times 10^{-3}$	$2.0 \times 10^{-3}$	5.25	−1.4
$2.5 \times 10^{-3}$	$2.5 \times 10^{-3}$	5.33	−1.5
$3.0 \times 10^{-3}$	$3.0 \times 10^{-3}$	5.22	−1.4

**Table 5** Experimental data concerning determination of  $\log K_{\text{ex}}$  ( $\text{TI}^+$ ,  $\mathbf{1}\cdot\text{Cs}^+$ ) on the basis of Eq. (5) for  $\text{M}^+=\text{TI}^+$ 

$\text{C}_{\text{TINO}_3}^{\text{in, aq}}$ (M)	$\text{C}_{\text{CsDCC}}^{\text{in, nb}}$ (M)	$D_{\text{Cs}}$	$\log K_{\text{ex}} (\text{TI}^+, \mathbf{1}\cdot\text{Cs}^+)$
$1.0 \times 10^{-3}$	$1.0 \times 10^{-3}$	0.52	0.6
$1.5 \times 10^{-3}$	$1.5 \times 10^{-3}$	0.54	0.5
$2.0 \times 10^{-3}$	$2.0 \times 10^{-3}$	0.55	0.5
$2.5 \times 10^{-3}$	$2.5 \times 10^{-3}$	0.60	0.4
$3.0 \times 10^{-3}$	$3.0 \times 10^{-3}$	0.57	0.5

**Table 6** Equilibrium data for the  $\text{M}^+$  and  $\mathbf{1}\cdot\text{M}^+$  cations in the two-phase water–nitrobenzene extraction system at 25 °C ( $\text{M}^+ = \text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ ,  $\text{Ag}^+$ ,  $\text{TI}^+$ ;  $\mathbf{1}$  = calix[4]arene-bis(coumarin-crown-6); for the meaning of the constants, see text)

Quantity	$\text{M}^+$					
	$\text{NH}_4^+$	$\text{K}^+$	$\text{Rb}^+$	$\text{Cs}^+$	$\text{Ag}^+$	$\text{TI}^+$
$\log K_{\text{M}^+}^{\text{I}}$	−4.7 <sup>a</sup>	−4.1 <sup>a</sup>	−3.4 <sup>a</sup>	−2.7 <sup>a</sup>	−4.5 <sup>b</sup>	−3.4 <sup>b</sup>
$\log K_{\text{ex}} (\text{M}^+, \text{Cs}^+)^{\text{c}}$	−2.0	−1.4	−0.7	−	−1.8	−0.7
$\log K_{\text{ex}} (\text{M}^+, \mathbf{1}\cdot\text{Cs}^+)^{\text{d, e}}$	−4.3	−1.8	−0.8	−	−1.4	0.5
$\log \beta_{\text{nb}} (\mathbf{1}\cdot\text{M}^+)^{\text{e, f}}$	6.1	8.0	8.3	8.4 <sup>g</sup>	8.8	9.6

<sup>a</sup> Ref. [25]

<sup>b</sup> Ref. [26]

<sup>c</sup> Calculated from Eq. 2 using data from Refs. [25, 26]

<sup>d</sup> Calculated from Eq. 5

<sup>e</sup> The standard deviations of the constants  $\log K_{\text{ex}} (\text{M}^+, \mathbf{1}\cdot\text{Cs}^+)$  and  $\log \beta_{\text{nb}} (\mathbf{1}\cdot\text{M}^+)$  are lower than 0.1

<sup>f</sup> Calculated from Eq. 6 using data from Refs. [25, 26, 30]

<sup>g</sup> Ref. [30]

In this work, from the extraction experiments and  $\gamma$ -activity measurements (see “Experimental” section) by means of Eq 5, the logarithms of the constants  $K_{\text{ex}}$  ( $\text{M}^+$ ,  $\mathbf{1}\cdot\text{Cs}^+$ ) were determined for  $\text{M}^+ = \text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Ag}^+$ , and  $\text{Tl}^+$ , as given in Tables 1, 2, 3, 4 and 5 and also in Table 6. In this context we must emphasize that these constants experimentally prove the justifying of the general extraction mechanism, the binding stoichiometry, and the presentation of the corresponding species, expressed by the two-phase chemical equilibrium (3).

Moreover, with respect to Refs. [27–29], for the extraction constants  $K_{\text{ex}}$  ( $\text{M}^+$ ,  $\text{Cs}^+$ ) and  $K_{\text{ex}}$  ( $\text{M}^+$ ,  $\mathbf{1}\cdot\text{Cs}^+$ ) defined above, as well as for the stability constants of the complexes  $\mathbf{1}\cdot\text{M}^+$  and  $\mathbf{1}\cdot\text{Cs}^+$  in nitrobenzene saturated with water, denoted by  $\beta_{\text{nb}}$  ( $\mathbf{1}\cdot\text{M}^+$ ) and  $\beta_{\text{nb}}$  ( $\mathbf{1}\cdot\text{Cs}^+$ ), respectively, one gets

$$\begin{aligned} \log \beta_{\text{nb}}(\mathbf{1}\cdot\text{M}^+) &= \log \beta_{\text{nb}}(\mathbf{1}\cdot\text{Cs}^+) + \log K_{\text{ex}}(\text{M}^+, \mathbf{1}\cdot\text{Cs}^+) \\ &\quad - \log K_{\text{ex}}(\text{M}^+, \text{Cs}^+) \end{aligned} \quad (6)$$

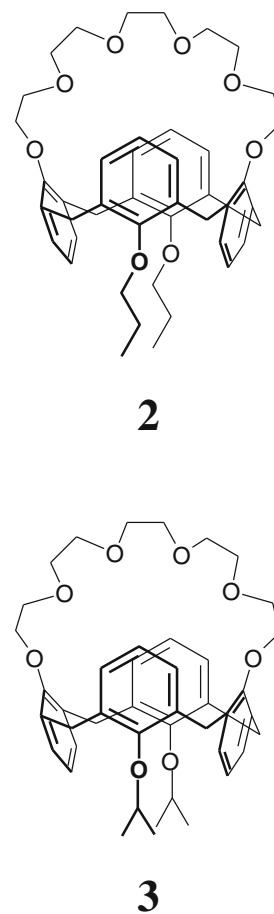
Finally, using the constants  $\log K_{\text{ex}}$  ( $\text{M}^+$ ,  $\text{Cs}^+$ ) and  $\log K_{\text{ex}}$  ( $\text{M}^+$ ,  $\mathbf{1}\cdot\text{Cs}^+$ ) given in Table 6,  $\log \beta_{\text{nb}}(\mathbf{1}\cdot\text{Cs}^+) = 8.4$  [30], determined from the distribution of cesium iodide in the water–nitrobenzene system containing the investigated ligand **1**, and applying Eq. 6, the stability constants of the  $\mathbf{1}\cdot\text{M}^+$  complexes ( $\text{M}^+ = \text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Ag}^+$ ,  $\text{Tl}^+$ ) in water-saturated nitrobenzene were evaluated. These data are also summarized in Table 6. Thus, the  $\log \beta_{\text{nb}}(\mathbf{1}\cdot\text{M}^+)$  values from this table, as well as the values of  $\log \beta_{\text{nb}}(\mathbf{1}\cdot\text{Li}^+) = 4.3 \pm 0.1$ ,  $\log \beta_{\text{nb}}(\mathbf{1}\cdot\text{Na}^+) = 4.5 \pm 0.1$ , and  $\log \beta_{\text{nb}}(\mathbf{1}\cdot\text{H}_3\text{O}^+) = 4.2 \pm 0.1$  [30], indicate that the stability of the  $\mathbf{1}\cdot\text{M}^+$  cationic complex species in the mentioned nitrobenzene medium increases in the following cation order:  $\text{H}_3\text{O}^+ < \text{Li}^+ < \text{Na}^+ < \text{NH}_4^+ < \text{K}^+ < \text{Rb}^+ < \text{Cs}^+ < \text{Ag}^+ < \text{Tl}^+$ . Hence, from this point of view, the investigated ligand **1** cannot be considered in nitrobenzene saturated with water as a cesium receptor only, but predominantly as an extraordinarily effective receptor for the very “soft” cations  $\text{Ag}^+$  and  $\text{Tl}^+$ . Further, as follows from Table 7, the stability constants of the  $\mathbf{2}\cdot\text{M}^+$  and  $\mathbf{3}\cdot\text{M}^+$  cationic complexes, where  $\text{M}^+ = \text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ , or  $\text{Cs}^+$  and **2** and **3** denote 1,3-*alternate*-25,27-dipropoxycalix[4]arene-crown-6 and 1,3-*alternate*-25,27-diisopropoxycalix[4]arene-crown-6, respectively (see Scheme 2), increase in both cases in the series of  $\text{Na}^+ < \text{K}^+ < \text{Rb}^+ < \text{Cs}^+$ . Besides, it is necessary to emphasize that the stability constants of the  $\mathbf{1}\cdot\text{M}^+$  complexes ( $\text{M}^+ = \text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ ) in water-saturated nitrobenzene are substantially higher than those of the corresponding cationic complexes  $\mathbf{2}\cdot\text{M}^+$  and  $\mathbf{3}\cdot\text{M}^+$  determined in methanol [7]. On the other hand, the  $\text{Cs}^+/\text{Na}^+$  and  $\text{Cs}^+/\text{K}^+$  selectivities in the methanolic medium in the presence of the ligand **2** or ligand **3**, respectively, are

**Table 7** Stability constants of the  $\mathbf{2}\cdot\text{M}^+$  and  $\mathbf{3}\cdot\text{M}^+$  complex cations ( $\mathbf{2}$ =1,3-*alternate*-25,27-dipropoxycalix[4]arene-crown-6,  $\mathbf{3}$ =1,3-*alternate*-25,27-diisopropoxycalix[4]arene-crown-6;  $\text{M}^+=\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ ) in methanol at 25 °C (according to Ref. [7])

$\text{M}^+$	$\text{Na}^+$	$\text{K}^+$	$\text{Rb}^+$	$\text{Cs}^+$
$\log \beta_{\text{CH}_3\text{OH}}(\mathbf{2}\cdot\text{M}^+)^a$	$\leq 1$	$4.3 \pm 0.2$	$5.96 \pm 0.01$	$6.4 \pm 0.2$
$\log \beta_{\text{CH}_3\text{OH}}(\mathbf{3}\cdot\text{M}^+)^a$	$\leq 1$	$4.5 \pm 0.1$	$5.93 \pm 0.06$	$6.1 \pm 0.2$

<sup>a</sup> Ref. [7]

**Scheme 2** Structural formulas of 1,3-*alternate*-25,27-dipropoxycalix[4]arene-crown-6 (abbrev. **2**) and 1,3-*alternate*-25,27-diisopropoxycalix[4]arene-crown-6 (abbrev. **3**)



considerably higher than the mentioned selectivities in the nitrobenzene medium containing the investigated ligand **1**. It means that in these or similar cases, especially the solvent (of course, in addition to the structure of the ligand studied) can play the very important role.

In conclusion, it should be noted that in the case of cyclic polyether compounds with oxyethylene groups –  $\text{CH}_2\text{--CH}_2\text{--O--}$ , that are called crowns owing to their structure [31, 32], as well as in the case of valinomycin [33, 34], the ratio of the size of ligand cavity to the ion radius of the central cation, the number and arrangements of the ligand binding sites, the substitution on the macrocyclic

rings, and the solvent effects can be important factors in the stability of the complex species formed [35]. However, the use of the cavity size as the sole criteria for the design of complementary ligand architecture often fails [36]. On the other hand, in this case of the cationic complexes  $1\cdot M^+$  under consideration involving the substituted calix[4]arene receptor **1**, cation- $\pi$  interaction (of course, together with coordination by means of the six ether oxygens from the substituted crown-6 moiety) evidently plays the crucial role in the stability of these univalent complex species  $1\cdot M^+$ . Therefore, the stability constants of the  $1\cdot M^+$  complexes with the very “hard” cations (i.e.,  $Li^+$ ,  $Na^+$ , or  $H_3O^+$ ) are substantially lower than those involving the very “soft” cations (i.e.,  $Ag^+$  or especially  $Tl^+$ ), as follows from the series presented above.

**Acknowledgments** This work was supported by the Grant Agency of Faculty of Environmental Sciences, Czech University of Life Sciences, Prague, Project No.: 42900/1312/3114 “Environmental Aspects of Sustainable Development of Society,” and by the Czech Ministry of Education, Youth, and Sports (Project MSM 6046137307).

## References

- Böhmer, V.: Calixarenes, macrocycles with (almost) unlimited possibilities. *Angew. Chem. Int. Ed.* **34**, 713–745 (1995)
- Alfieri, C., Dradi, E., Pochini, A., Ungaro, R., Andreetti, G.D.: Synthesis, and X-ray crystal and molecular structure of a novel macro-bicyclic ligand: crowned *p*-*t*-butyl-calix[4]arene. *J. Chem. Soc. Chem. Commun.* **19**, 1075–1077 (1983)
- Asfari, Z., Wenger, S., Vicens, J.: Calixcrowns and related molecules. *J. Incl. Phenom.* **19**, 137–148 (1994)
- Kim, J.S., Vicens, J.: Progress of calixcrowns chemistry. *J. Incl. Phenom. Macrocycl. Chem.* **63**, 189–193 (2009)
- Gutsche, C.D.: *Calixarenes Revisited*. The Royal Society of Chemistry, Cambridge (1998)
- Ungaro, R., Casnati, A., Ugozzoli, F., Pochini, A., Dozol, J.F., Hill, C., Rouquette, H.: 1,3-Dialkoxycalix[4]arene-crowns-6 in 1,3-alternate conformation: cesium-selective ligands that exploit cation-arene interactions. *Angew. Chem. Int. Ed.* **33**, 1506–1509 (1994)
- Casnati, A., Pochini, A., Ungaro, R., Ugozzoli, F., Arnaud, F., Fanni, S., Schwing, M.J., Egberink, R.J.M., de Jong, F., Reinholdt, D.N.: Synthesis, complexation, and membrane transport studies of 1,3-alternate calix[4]arene-crown-6 conformers: a new class of cesium selective ionophores. *J. Am. Chem. Soc.* **117**, 2767–2777 (1995)
- Thuéry, P., Nierlich, M., Bryan, J. C., Lamare, V., Dozol, J. F., Asfari, Z., Vicens, J.: Crown ether conformations in 1,3-calix[4]arene bis(crown ethers): crystal structures of a caesium complex and solvent adducts and molecular dynamics simulations. *J. Chem. Soc. Dalton Trans.* 4191–4202 (1997)
- Deng, Y., Sachleben, R.A., Moyer, B.A.: Equilibrium aspects of the extraction of caesium nitrate by dicyclohexano-21-crown-7, dibenzo-21-crown-7 and bis-[*tert*-alkylbenzo]-21-crown-7 in 1,2-dichloroethane. *J. Chem. Soc. Faraday Trans.* **91**, 4215–4222 (1995)
- Sachleben, R.A., Bonnesen, P.V., Descazeaud, T., Haverlock, T.J., Urvoas, A., Moyer, B.A.: Surveying the extraction of cesium nitrate by 1,3-alternate-calix[4]arene-crown-6 ethers in 1,2-dichloroethane. *Solvent Extr. Ion Exch.* **17**, 1445–1459 (1999)
- Haverlock, T.J., Bonnesen, P.V., Sachleben, R.A., Moyer, B.A.: Analysis of equilibria in the extraction of cesium nitrate by calix[4]arene-bis(*t*-octylbenzo-crown-6) in 1,2-dichloroethane. *J. Incl. Phenom. Macrocycl. Chem.* **36**, 21–37 (2000)
- Wintergerst, M.P., Levitskaia, T.G., Moyer, B.A., Sessler, J.L., Delmau, L.H.: Calix[4]pyrrole: a new ion-pair receptor as demonstrated by liquid–liquid extraction. *J. Am. Chem. Soc.* **130**, 4129–4139 (2008)
- Makrlík, E., Vaňura, P.: Applications of the dicarbollylcobaltate(III) anion in the water/nitrobenzene extraction system. *Talanta* **32**, 423–429 (1985)
- Makrlík, E., Vaňura, P., Selucký, P.: Stability constants of some univalent cation complexes of 2,3-naphtho-15-crown-5 in nitrobenzene saturated with water. *J. Solut. Chem.* **38**, 1129–1138 (2009)
- Makrlík, E., Vaňura, P., Selucký, P.: Solvent extraction of europium and americium into phenyltrifluoromethyl sulfone by using synergistic mixture of hydrogen dicarbollylcobaltate and “classical” CMPO. *J. Radioanal. Nucl. Chem.* **283**, 571–575 (2010)
- Toman, P., Makrlík, E., Vaňura, P., Kašička, V.: Protonation of benzo-18-crown-6: extraction and DFT study. *Z. Phys. Chem.* **225**, 265–270 (2011)
- Makrlík, E., Toman, P., Vaňura, P.: Experimental and theoretical study on the complexation of the cesium cation with dibenzo-30-crown-10. *J. Radioanal. Nucl. Chem.* **292**, 1137–1140 (2012)
- Makrlík, E., Spíchal, Z., Vaňura, P., Selucký, P.: Synergistic extraction of europium and americium into nitrobenzene by using hydrogen dicarbollylcobaltate and bis(diphenylphosphino)methane dioxide. *J. Radioanal. Nucl. Chem.* **295**, 2135–2140 (2013)
- Romanovskiy, V.N., Smirnov, I.V., Babain, V.A., Todd, T.A., Herbst, R.S., Law, J.D., Brewer, K.N.: The universal solvent extraction (UNEX) process. I. Development of the UNEX process solvent for the separation of cesium, strontium and the actinides from acidic radioactive waste. *Solvent Extr. Ion Exch.* **19**, 1–21 (2001)
- Law, J.D., Herbst, R.S., Todd, T.A., Romanovskiy, V.N., Babain, V.A., Esimantovskiy, V.M., Smirnov, I.V., Zaitsev, B.N.: The universal solvent extraction (UNEX) process. II. Flowsheet development and demonstration of the UNEX process for the separation of cesium, strontium and actinides from actual acidic radioactive waste. *Solvent Extr. Ion Exch.* **19**, 23–36 (2001)
- Herbst, R.S., Peterman, D.R., Tillotson, R.D., Delmau, L.H.: Fundamental chemistry of cesium extraction from acidic media by HCCD in FS-13. *Solvent Extr. Ion Exch.* **26**, 163–174 (2008)
- Leray, I., Asfari, Z., Vicens, J., Valeur, B.: Photophysics of calix[4]biscrown-based ditopic receptors of caesium containing one or two dioxocoumarin fluorophores. *J. Fluoresc.* **14**, 451–458 (2004)
- Leray, I., Asfari, Z., Vicens, J., Valeur, B.: Synthesis and binding properties of calix[4]biscrown-based fluorescent molecular sensors for caesium or potassium ions. *J. Chem. Soc. Perkin Trans. 2*, 1429–1434 (2002)
- Hawthorne, M.F., Young, D.C., Andrews, T.D., Howe, D.V., Pilling, R.L., Pitts, A.D., Reintjes, M., Warren Jr, L.F., Wegner, P.A.:  $\pi$ -Dicarbollyl derivatives of the transition metals: metallocene analogs. *J. Am. Chem. Soc.* **90**, 879–896 (1968)
- Rais, J.: Individual extraction constants of univalent ions in the system water-nitrobenzene. *Collect. Czech. Chem. Commun.* **36**, 3253–3262 (1971)
- Makrlík, E., Božek, F.: Individual extraction constants of some univalent cations in the water-nitrobenzene system. *Polish J. Chem.* **72**, 949–952 (1998)



27. Daňková, M., Makrlík, E., Vaňura, P.: Stability of the valinomycin—rubidium complex in water saturated nitrobenzene. *J. Radioanal. Nucl. Chem.* **221**, 251–253 (1997)
28. Makrlík, E., Vaňura, P.: Extraction of sodium picrate into nitrobenzene in the presence of valinomycin. *ACH - Models Chem.* **135**, 213–218 (1998)
29. Makrlík, E., Vaňura, P.: Experimental evidence for a valinomycin - proton complex. *Monatsh. Chem.* **137**, 157–161 (2006)
30. Makrlík, E., Vaňura, P., Asfari, Z.: Unpublished results
31. Pedersen, C.J.: Cyclic polyethers and their complexes with metal salts. *J. Am. Chem. Soc.* **89**, 2495–2496 (1967)
32. Pedersen, C.J.: Cyclic polyethers and their complexes with metal salts. *J. Am. Chem. Soc.* **89**, 7017–7036 (1967)
33. Hofmanová, A., Koryta, J., Březina, M., Ryan, T.H., Angelis, K.: Electrochemical reduction of monovalent cation complexes of macrocyclic ionophores. II. Valinomycin and macrotetrolide complexes. *Inorg. Chim. Acta* **37**, 135–140 (1979)
34. Ehala, S., Kašička, V., Makrlík, E.: Determination of stability constants of valinomycin complexes with ammonium and alkali metal ions by capillary affinity electrophoresis. *Electrophoresis* **29**, 652–657 (2008)
35. Kolthoff, I.M.: Application of macrocyclic compounds in chemical analysis. *Anal. Chem.* **51**, 1R–22R (1979)
36. Hay, B.P., Hancock, R.D.: The role of donor group orientation as a factor in metal ion recognition by ligands. *Coord. Chem. Rev.* **212**, 61–78 (2001)