

# On the complexation of some univalent cations with 1,3-*alternate*-25,27-bis(1-octyloxy)calix[4]arene-crown-6 in nitrobenzene saturated with water

Emanuel Makrlík · Pavel Selucký · Petr Vaňura

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**Abstract** From extraction experiments and  $\gamma$ -activity measurements, the exchange extraction constants corresponding to the general equilibrium  $M^+ (aq) + 1 \cdot Cs^+ (nb) \rightleftharpoons 1 \cdot M^+ (nb) + Cs^+ (aq)$  taking place in the two-phase water–nitrobenzene system ( $M^+ = Ag^+, K^+, Rb^+, Tl^+$ ; **1** = 1,3-*alternate*-25,27-bis(1-octyloxy)calix[4]arene-crown-6; aq is aqueous phase, nb is nitrobenzene phase) were determined. Moreover, the stability constants of the **1**· $M^+$  complexes in water-saturated nitrobenzene were calculated; they were found to increase in the series of  $K^+ < Rb^+ < Ag^+ < Tl^+$ .

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

## Introduction

The dicarbollylcobaltate anion ( $DCC^-$ ) [1] and some of its halogen derivatives are very useful reagents for the

extraction of various metal cations (especially  $Cs^+$ ,  $Sr^{2+}$ ,  $Ba^{2+}$ ,  $Eu^{3+}$ , and  $Am^{3+}$ ) from aqueous solutions into a polar organic phase, both under laboratory conditions for purely theoretical or analytical purposes [2–6], and on the technological scale for the separation of some high-activity isotopes in the reprocessing of spent nuclear fuel and acidic radioactive waste [7–9].

Calixarenes are macrocyclic compounds which are not only easily available on a large scale, but also offer nearly boundless possibilities for chemical modification [10]. This makes them highly attractive as 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 [11], but also elegantly demonstrate the potential of these compounds [12]. Calixarenes find applications as selective binders and carriers, as analytical sensors, as catalysts and model structures for biomimetic studies [13].

New cesium selective extractants especially from the calix[4]arene-crown-6 and calix[4]arene-bis(crown-6) families have been introduced [14–20]. The corresponding crystal structures of model complexes with cesium salts have demonstrated a significant  $\pi$ -interaction between the facing aromatic rings and the  $Cs^+$  guest cation [14–16]. Besides, calix[4]arene-crown-6 family of the mentioned compounds gives  $Cs^+/Na^+$  separation factors exceeding  $10^4$  [15].

Recently, interaction of the  $H_3O^+$  cation with 1,3-*alternate*-25,27-bis(1-octyloxy)calix[4]arene-crown-6 (abbrev. **1**; see Scheme 1) has been investigated by an extraction method and theoretical quantum–mechanical DFT calculations [21]. On the other hand, in the current work, the solvent extraction of  $Ag^+$ ,  $K^+$ ,  $Rb^+$ , and  $Tl^+$  into nitrobenzene by means of a synergistic mixture of cesium dicarbollylcobaltate [1] and the mentioned receptor **1** was

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

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

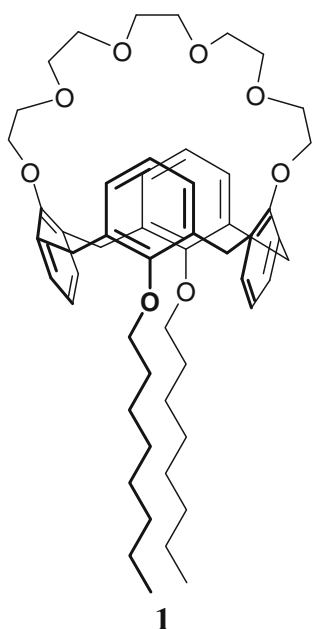
P. Vaňura  
Department of Analytical Chemistry, Institute of Chemical Technology, Prague, Technická 5, 166 28 Prague 6, Czech Republic  
e-mail: petr.vanura@vscht.cz

studied. Further, the stability constants of the proved univalent cationic complexes with this substituted calix[4]arene electroneutral species **1** were determined in the organic phase of the water–nitrobenzene extraction system. Finally, the stability constants of the considered  $1 \cdot M^+$  complexes involving the very “hard” and “soft” cations were compared and discussed.

## Experimental

Compound **1** (see Scheme 1) was kindly supplied by Prof. V. I. Kalchenko, Institute of Organic Chemistry, NASU, Kiev, Ukraine. Cesium dicarbollylcobaltate (CsDCC) was synthesized by means of the method published by Hawthorne et al. [22]. The other chemicals used (Lachema, Brno, Czech Republic) were of reagent grade purity. The radionuclide  $^{137}\text{Cs}^+$  was purchased from Technavekspport, Russia.

The extraction experiments were carried out in 10 mL glass test-tubes with polyethylene stoppers: 2 mL of an aqueous solution of  $\text{MNO}_3$  ( $M^+ = \text{Ag}^+, \text{K}^+, \text{Rb}^+, \text{TI}^+$ ) 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, the initial concentrations of which also varied 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 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



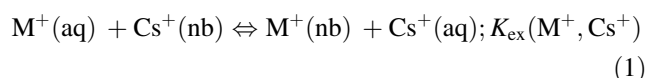
**Scheme 1** Structural formula of 1,3-alternate-25,27-bis(1-octyloxy)calix[4]arene-crown-6 (abbrev. **1**)

$25 \pm 1$  °C, using a laboratory shaker. Then the phases were separated by centrifugation. Afterwards, 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 NK 350 (Gamma, Budapest, Hungary).

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

## Results and discussion

Regarding the results of previous papers [1, 23, 24], the two-phase water– $\text{MNO}_3$  ( $M^+ = \text{Ag}^+, \text{K}^+, \text{Rb}^+, \text{TI}^+$ )–nitrobenzene–cesium dicarbollylcobaltate (CsDCC) extraction system can be described by the following equilibrium



with the corresponding exchange extraction constant  $K_{\text{ex}}(M^+, \text{Cs}^+)$ ; aq and nb denote the presence of the species in the aqueous and nitrobenzene phases, respectively. For the constant  $K_{\text{ex}}(M^+, \text{Cs}^+)$  one can write [1, 23, 24]

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

where  $K_{M^+}^i$  and  $K_{\text{Cs}^+}^i$  are the individual extraction constants for  $M^+$  and  $\text{Cs}^+$ , respectively, in the water–nitrobenzene system [23, 24]. Knowing the values  $\log K_{M^+}^i$  ( $M^+ = \text{Ag}^+, \text{K}^+, \text{Rb}^+, \text{TI}^+, \text{Cs}^+$ ) [23, 24], the single exchange extraction constants  $K_{\text{ex}}(M^+, \text{Cs}^+)$  were simply calculated from Eq. 2. The corresponding data are given in Table 1.

**Table 1** Equilibrium data for the  $M^+$  and  $1 \cdot M^+$  cations in the two-phase water–nitrobenzene extraction system at 25 °C ( $M^+ = \text{Ag}, \text{K}^+, \text{Rb}^+, \text{TI}^+$ ; **1** = 1,3-alternate-25,27-bis(1-octyloxy)calix[4]arene-crown-6; for the meaning of the constants see text)

Quantity	$M^+$				
	$\text{Ag}^+$	$\text{K}^+$	$\text{Rb}^+$	$\text{TI}^+$	$\text{Cs}^+$
$\log K_{M^+}^i$ <sup>a</sup>	−4.5 <sup>b</sup>	−4.1 <sup>a</sup>	−3.4 <sup>a</sup>	−3.4 <sup>b</sup>	−2.7 <sup>a</sup>
$\log K_{\text{ex}}(M^+, \text{Cs}^+)$ <sup>c</sup>	−1.8	−1.4	−0.7	−0.7	−
$\log K_{\text{ex}}(M^+, 1 \cdot \text{Cs}^+)$ <sup>d,f</sup>	−1.0	−1.8	−0.9	2.1	−
$\log \beta_{\text{nb}}(1 \cdot M^+)$ <sup>e,f</sup>	9.6	8.4	8.6	11.6	8.8 <sup>g</sup>

<sup>a</sup> Ref. [23]

<sup>b</sup> Ref. [24]

<sup>c</sup> Calculated from Eq. 2 using data from Refs. [23, 24]

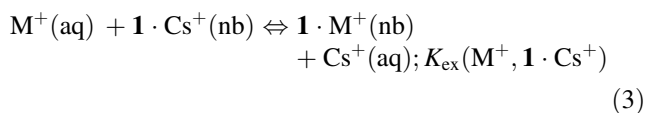
<sup>d</sup> Calculated from Eq. 5

<sup>e</sup> Calculated from Eq. 6 using data from Refs. [23, 24, 28]

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

<sup>g</sup> Ref. [28]

Previous results [24–27] indicated that the two-phase water–MNO<sub>3</sub> (M<sup>+</sup> = Ag, K<sup>+</sup>, Rb<sup>+</sup>, Tl<sup>+</sup>)-nitrobenzene-**1**-CsDCC extraction system (see “Experimental” Section), chosen for determination of the stability constant of the **1**·M<sup>+</sup> complex in nitrobenzene saturated with water, can be characterized by the main chemical equilibrium (3):



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

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

It is necessary to emphasize that **1** is a considerably hydrophobic ligand, practically present in the nitrobenzene phase only, where it forms the very stable complexes **1**·M<sup>+</sup> and **1**·Cs<sup>+</sup> with the mentioned univalent cations. Taking into account 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 obtain the final expression for  $K_{\text{ex}}(\text{M}^+, \mathbf{1} \cdot \text{Cs}^+)$  in the form

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

where  $C_{\text{MNO}_3}^{\text{in,aq}}$  is the initial concentration of MNO<sub>3</sub> (M<sup>+</sup> = Ag<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup>, Tl<sup>+</sup>) in the aqueous phase and  $C_{\text{CsDCC}}^{\text{in,nb}}$  denotes the initial concentration of CsDCC in the organic phase of the system under consideration.

In this study, 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, as given in Table 1.

Moreover, with respect to Refs. [25–27], 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 **1**·M<sup>+</sup> and **1**·Cs<sup>+</sup> 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

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

Finally, by using the values of  $\log K_{\text{ex}}(\text{M}^+, \text{Cs}^+)$  and  $\log K_{\text{ex}}(\text{M}^+, \mathbf{1} \cdot \text{Cs}^+)$  given in Table 1,  $\log \beta_{\text{nb}}(\mathbf{1} \cdot \text{Cs}^+) = 8.8$  [28], and applying Eq. 6, the stability

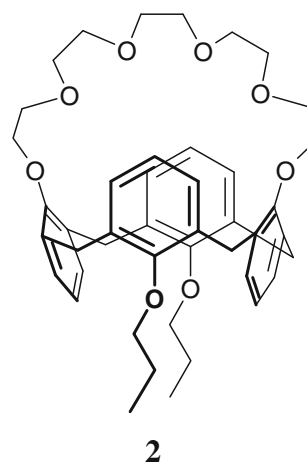
constants of the **1**·M<sup>+</sup> complexes (M<sup>+</sup> = Ag<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup>, Tl<sup>+</sup>) in water-saturated nitrobenzene were evaluated. These data are also listed in Table 1. Thus, the  $\log \beta_{\text{nb}}(\mathbf{1} \cdot \text{M}^+)$  values from this table, as well as the values of  $\log \beta_{\text{nb}}(\mathbf{1} \cdot \text{Na}^+) = 6.5 \pm 0.1$  and  $\log \beta_{\text{nb}}(\mathbf{1} \cdot \text{H}_3\text{O}^+) = 6.3 \pm 0.1$  determined previously [21], indicate that the stability of the **1**·M<sup>+</sup> cationic complex species in the mentioned nitrobenzene medium increases in the following cation order:  $\text{H}_3\text{O}^+ < \text{Na}^+ < \text{K}^+ < \text{Rb}^+ < \text{Cs}^+ < \text{Ag}^+ < \text{Tl}^+$ . In this context it should be noted that the stability constants of the **2**·M<sup>+</sup> complex cations, where **2** = 1,3-*alternate*-25,27-bis(1-propyloxy)calix[4]arene-crown-6 (see Scheme 2) and M<sup>+</sup> = Na<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup>, Cs<sup>+</sup>, reported for methanol [15], increase in the series of  $\text{Na}^+ < \text{K}^+ < \text{Rb}^+ < \text{Cs}^+$ , as follows from Table 2.

In conclusion, it should be noted that in the case of cyclic polyether compounds with oxyethylene groups –CH<sub>2</sub>–CH<sub>2</sub>–O–, that are called crowns owing to their structure [29, 30], as well as in the case of valinomycin [31, 32], the ratio of the size of the ligand cavity to the ion radius of the central cation, the number and arrangements of the ligand bonding sites, the substitution on the macrocyclic ring, and the solvent effects can be important factors in the stability of the complex species formed [33]. However, the use of the cavity size as the sole criteria for the design of complementary ligand architecture often fails [34]. On the other hand, in the case of the cationic

**Table 2** Stability constants of the **2**·M<sup>+</sup> complex cations in methanol at 25 °C (**2** = 1,3-*alternate*-25,27-bis(1-propyloxy)calix[4]arene-crown-6; M<sup>+</sup> = Na<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup>, Cs<sup>+</sup>) [15]

M <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Rb <sup>+</sup>	Cs <sup>+</sup>
$\log \beta_{\text{CH}_3\text{OH}}(\mathbf{2} \cdot \text{M}^+)^a$	≤1	4.3 ± 0.2	5.96 ± 0.01	6.4 ± 0.2

<sup>a</sup> Ref. [15]



**Scheme 2** Structural formula of 1,3-*alternate*-25,27-bis(1-propyloxy)calix[4]arene-crown-6 (abbrev. **2**)

complexes  $1 \cdot M^+$  under consideration involving the substituted calix[4]arene receptor **1**, cation  $\pi$ -interaction 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.,  $H_3O^+$  or  $Na^+$ ) are substantially lower than those involving the very “soft” cations (i.e.,  $Ag^+$  or especially  $Tl^+$ ), as follows from the series presented above.

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