

Short communication

# Solvent Extraction of Some Divalent Metal Cations into Nitrobenzene by Using a Synergistic Mixture of Strontium Dicarbolylcobaltate and *p*-*tert*-Butylcalix[4]arene-tetrakis(*N,N*-Diethylacetamide)

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Received: 14-03-2012

## Abstract

From extraction experiments and  $\gamma$ -activity measurements, the exchange extraction constants corresponding to the general equilibrium  $M^{2+}(aq) + 1 \cdot Sr^{2+}(nb) \rightleftharpoons 1 \cdot M^{2+}(nb) + Sr^{2+}(aq)$  taking place in the two-phase water–nitrobenzene system ( $M^{2+} = Ca^{2+}, Ba^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, UO_2^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}$ ; **1** = *p*-*tert*-butylcalix[4]arene-tetrakis(*N,N*-diethylacetamide)); aq = aqueous phase, nb = nitrobenzene phase) were determined. Further, the stability constants of the  $1 \cdot M^{2+}$  complexes in water-saturated nitrobenzene were calculated; they were found to increase in the series of  $Cu^{2+} < Ba^{2+} < Zn^{2+} < Ni^{2+} < UO_2^{2+} < Co^{2+} < Mn^{2+} < Cd^{2+} < Ca^{2+} < Pb^{2+}$ .

**Keywords:** Divalent metal cations, substituted calix[4]arene, complexation, extraction and stability constants, water-nitrobenzene system

## 1. Introduction

The dicarbolylcobaltate anion ( $DCC^-$ )<sup>1</sup> 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,<sup>2–14</sup> and on the technological scale for the separation of some high-activity isotopes in the reprocessing of spent nuclear fuel and acidic radioactive waste.<sup>15–17</sup>

Calix[n]arenes are a well – known family of macrocyclic molecules with many potential applications in various branches of chemistry. Because of their simple one-pot preparation, easy derivatization and unique complexation abilities, calix[n]arenes are widely used as the building blocks for the constructions of more sophisticated molecular systems. Their unique three-dimensional

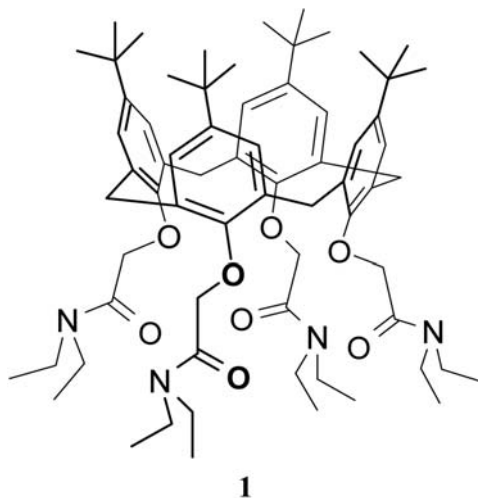
pre-organization make them very attractive as the receptors for the complexation of cations, anions, and even neutral molecules. Calix[n]arenes find applications as selective binders and carriers, as analytical sensors, as catalysts and model structures for biomimetic studies.<sup>18,19</sup> In the field of host-guest chemistry, many studies have focused on the binding ability of calixarene derivatives with carbonyl groups at their lower rims toward metal ions, predominantly alkali and alkaline-earth, but also transition and heavy metal cations.<sup>20–30</sup>

In the current work, the synergistic extraction of  $Ca^{2+}$ ,  $Ba^{2+}$ ,  $Cu^{2+}$ ,  $Zn^{2+}$ ,  $Cd^{2+}$ ,  $Pb^{2+}$ ,  $UO_2^{2+}$ ,  $Mn^{2+}$ ,  $Co^{2+}$  and  $Ni^{2+}$  into nitrobenzene by means of strontium dicarbolylcobaltate,  $Sr(DCC)_2$ , and *p*-*tert*-butylcalix[4]arene-tetrakis(*N,N*-diethylacetamide) (abbrev. **1**; see Scheme 1) was investigated. Moreover, the stability constants of the proved divalent metal cation complexes of the mentioned substituted calix[4]arene ligand **1** were evaluated in the

organic phase of the water-nitrobenzene extraction system.

## 2. Experimental

Electroneutral compound **1** (see Scheme 1) was synthesized by the method published in Ref. 31. Cesium dicarbollycobaltate (CsDCC) was prepared by means of the method published by Hawthorne et al.<sup>32</sup> The other chemicals used (Lachema, Brno, Czech Republic) were of reagent grade purity. A nitrobenzene solution of hydrogen dicarbollycobaltate (HDCC)<sup>1</sup> was prepared from CsDCC by the procedure described elsewhere.<sup>33</sup> The equilibration of the nitrobenzene solution of HDCC with stoichiometric Sr(OH)<sub>2</sub>, which was dissolved in an aqueous solution of Sr(NO<sub>3</sub>)<sub>2</sub> (0.20 mol/L), yielded the corresponding Sr(DCC)<sub>2</sub> solution in nitrobenzene. The radionuclide <sup>85</sup>Sr<sup>2+</sup> was supplied by DuPont, Belgium.



**Scheme 1.** Structural formula of a *p*-*tert*-butylcalix[4]arene-tetrakis(*N,N*-diethylacetamide) (abbrev. **1**).

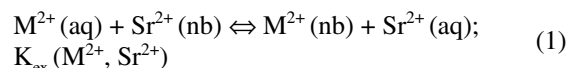
The extraction experiments were carried out in 10 mL polypropylene test-tubes with polypropylene stoppers: 2 mL of an aqueous solution of M(NO<sub>3</sub>)<sub>2</sub> (M<sup>2+</sup> = Ca<sup>2+</sup>, Ba<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>, Pb<sup>2+</sup>, UO<sub>2</sub><sup>2+</sup>, Mn<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>) of the con-

centration in the range from 1 × 10<sup>-3</sup> to 5 × 10<sup>-3</sup> mol/L and microamounts of <sup>85</sup>Sr<sup>2+</sup> were added to 2 mL of a nitrobenzene solution of **1** and Sr(DCC)<sub>2</sub>, whose initial concentrations also varied from 1 × 10<sup>-3</sup> to 5 × 10<sup>-3</sup> mol/L (in all experiments, the initial concentration of **1** in nitrobenzene, C<sub>1</sub><sup>in,nb</sup>, was always equal to the initial concentration of Sr(DCC)<sub>2</sub> in this medium, C<sub>Sr(DCC)<sub>2</sub></sub><sup>in,nb</sup>). The test-tubes filled with the solutions were shaken for 12 h at 25 ± 1 °C, using a laboratory shaker. Then the phases were separated by centrifugation. Afterwards, 1 mL samples were taken from each phase and their γ-activities were measured by means of a well-type NaI(Tl) scintillation detector connected to a γ-analyzer NK 350 (Gamma, Budapest, Hungary).

The equilibrium distribution ratios of strontium, D<sub>Sr</sub>, were determined as the ratios of the corresponding measured radioactivities of <sup>85</sup>Sr<sup>2+</sup> in the nitrobenzene and aqueous samples.

## 3. Results and Discussion

Regarding the results of previous papers,<sup>1,34</sup> the two-phase water–M(NO<sub>3</sub>)<sub>2</sub> (M<sup>2+</sup> = Ca<sup>2+</sup>, Ba<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>, Pb<sup>2+</sup>, UO<sub>2</sub><sup>2+</sup>, Mn<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>)–nitrobenzene–Sr(DCC)<sub>2</sub> extraction system can be described by the following equilibrium



with the corresponding exchange extraction constant K<sub>ex</sub>(M<sup>2+</sup>, Sr<sup>2+</sup>); aq and nb denote the presence of the species in the aqueous and nitrobenzene phases, respectively. For the constant K<sub>ex</sub>(M<sup>2+</sup>, Sr<sup>2+</sup>) one can write<sup>1,34</sup>

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

where K<sub>M<sup>2+</sup></sub><sup>i</sup> and K<sub>Sr<sup>2+</sup></sub><sup>i</sup> are the individual extraction constants for M<sup>2+</sup> and Sr<sup>2+</sup>, respectively, in the water-nitrobenzene system.<sup>34</sup> Knowing the values of log K<sub>M<sup>2+</sup></sub><sup>i</sup> (M<sup>2+</sup> = Ca<sup>2+</sup>, Sr<sup>2+</sup>, Ba<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>, Pb<sup>2+</sup>, UO<sub>2</sub><sup>2+</sup>, Mn<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>),<sup>34</sup> the single exchange extraction constants K<sub>ex</sub>(M<sup>2+</sup>, Sr<sup>2+</sup>) were simply calculated from Eq. (2). The corresponding data are given in Table 1.

**Table 1.** Equilibrium data for the M<sup>2+</sup> and 1·M<sup>2+</sup> cations in the two-phase water–nitrobenzene extraction system at 25 °C (M<sup>2+</sup> = Ca<sup>2+</sup>, Sr<sup>2+</sup>, Ba<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>, Pb<sup>2+</sup>, UO<sub>2</sub><sup>2+</sup>, Mn<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>; **1** = *p*-*tert*-butylcalix[4]arene-tetrakis(*N,N*-diethylacetamide)); for the meaning of the constants see text).

Quantity	M <sup>2+</sup>										
	Ca <sup>2+</sup>	Sr <sup>2+</sup>	Ba <sup>2+</sup>	Cu <sup>2+</sup>	Zn <sup>2+</sup>	Cd <sup>2+</sup>	Pb <sup>2+</sup>	UO <sub>2</sub> <sup>2+</sup>	Mn <sup>2+</sup>	Co <sup>2+</sup>	Ni <sup>2+</sup>
log K <sub>M<sup>2+</sup></sub> <sup>i</sup> <sup>a</sup>	-11.2	-10.7	-10.5	-11.5	-11.6	-11.5	-10.6	-11.8	-11.1	-11.4	-11.6
log K <sub>ex</sub> (M <sup>2+</sup> , Sr <sup>2+</sup> ) <sup>b</sup>	-0.5	–	0.2	-0.8	-0.9	-0.8	0.1	-1.1	-0.4	-0.7	-0.9
log K <sub>ex</sub> (M <sup>2+</sup> , 1·Sr <sup>2+</sup> ) <sup>c</sup>	4.0	–	1.9	0.7	0.9	3.0	6.2	1.7	3.0	2.6	1.0
log β <sub>nb</sub> (1·M <sup>2+</sup> ) <sup>d</sup>	19.7	15.2 <sup>e</sup>	16.9	16.7	17.0	19.0	21.3	18.0	18.6	18.5	17.1

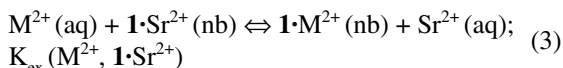
<sup>a</sup> Ref. 34; <sup>b</sup> Calculated from Eq. (2) using data from Ref. 34; <sup>c</sup> Calculated from Eq. (5); <sup>d</sup> Calculated from Eq. (6) using data from Refs. 34 and 40; <sup>e</sup> Ref. 40.

**Table 2.** Stability constants of the complexes  $2\cdot M^{2+}$ ,  $3\cdot M^{2+}$ ,  $4\cdot M^{2+}$  and  $5\cdot M^{2+}$  ( $M^{2+} = Ca^{2+}, Sr^{2+}, Ba^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, UO_4^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}$ ; structural formulas of the substituted calix[4]arene ligands **2**, **3**, **4** and **5** are presented in Scheme 2) in nitrobenzene saturated with water at 25 °C.

Quantity	$M^{2+}$										
	$Ca^{2+}$	$Sr^{2+}$	$Ba^{2+}$	$Cu^{2+}$	$Zn^{2+}$	$Cd^{2+}$	$Pb^{2+}$	$UO_4^{2+}$	$Mn^{2+}$	$Co^{2+}$	$Ni^{2+}$
$\log \beta_{nb}(2\cdot M^{2+})$	8.0 <sup>b</sup>	6.2 <sup>a</sup>	6.6 <sup>a</sup>	6.3 <sup>b</sup>	6.8 <sup>b</sup>	5.8 <sup>a</sup>	7.7 <sup>a</sup>	7.0 <sup>b</sup>	6.0 <sup>b</sup>	6.2 <sup>b</sup>	7.0 <sup>b</sup>
$\log \beta_{nb}(3\cdot M^{2+})$ <sup>c</sup>	8.6	7.1	6.2	6.8	6.8	6.9	6.7	7.2	6.5	6.7	6.9
$\log \beta_{nb}(4\cdot M^{2+})$ <sup>d</sup>	–	8.8	8.3	–	–	8.5	11.2	–	–	–	–
$\log \beta_{nb}(5\cdot M^{2+})$ <sup>e</sup>	10.2	8.7	8.0	8.5	8.6	8.6	11.3	8.6	8.0	8.2	8.5

<sup>a</sup> Ref. 41; <sup>b</sup> Ref. 42; <sup>c</sup> Ref. 43; <sup>d</sup> Ref. 44; <sup>e</sup> Ref. 45.

Previous results<sup>35–39</sup> indicated that the two-phase water –  $M(NO_3)_2$  ( $M^{2+} = Ca^{2+}, Ba^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, UO_4^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}$ ) – nitrobenzene – **1** (*p*-*tert*-butylcalix[4]arene-tetrakis(*N,N*-diethylacetamide)) –  $Sr(DCC)_2$  extraction system (see Experimental), chosen for determination of the stability constant of the  $1\cdot M^{2+}$  complex in nitrobenzene saturated with water, can be characterized by the main chemical equilibrium (3):



with the general equilibrium extraction constant  $K_{ex}(M^{2+}, 1\cdot Sr^{2+})$ :

$$K_{ex}(M^{2+}, 1\cdot Sr^{2+}) = \frac{[1\cdot M^{2+}]_{nb}[Sr^{2+}]_{aq}}{[M^{2+}]_{aq}[1\cdot Sr^{2+}]_{nb}} \quad (4)$$

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  $1\cdot M^{2+}$  with the mentioned divalent metal cations. Taking into account the conditions of electroneutrality in the organic and aqueous phases of the system under study, the mass balances of the divalent cations studied at equal volumes of the nitrobenzene and aqueous phases, as well as the measured equilibrium distribution ratio of strontium,  $D_{Sr} = [1\cdot Sr^{2+}]_{nb} / [Sr^{2+}]_{aq}$ , combined with Eq. (4), we obtain the final expression for  $K_{ex}(M^{2+}, 1\cdot Sr^{2+})$ :

$$K_{ex}(M^{2+}, 1\cdot Sr^{2+}) = \frac{1}{D_{Sr}} \times \frac{C_{Sr(DCC)_2}^{in,nb}}{(1 + D_{Sr}) C_{M(NO_3)_2}^{in,aq} - C_{Sr(DCC)_2}^{in,nb}} \quad (5)$$

where  $C_{M(NO_3)_2}^{in,aq}$  is the initial concentration of  $M(NO_3)_2$  ( $M^{2+} = Ca^{2+}, Ba^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, UO_4^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}$ ) in the aqueous phase and  $C_{Sr(DCC)_2}^{in,nb}$  denotes the initial concentration of  $Sr(DCC)_2$  in the organic phase of the system under consideration.

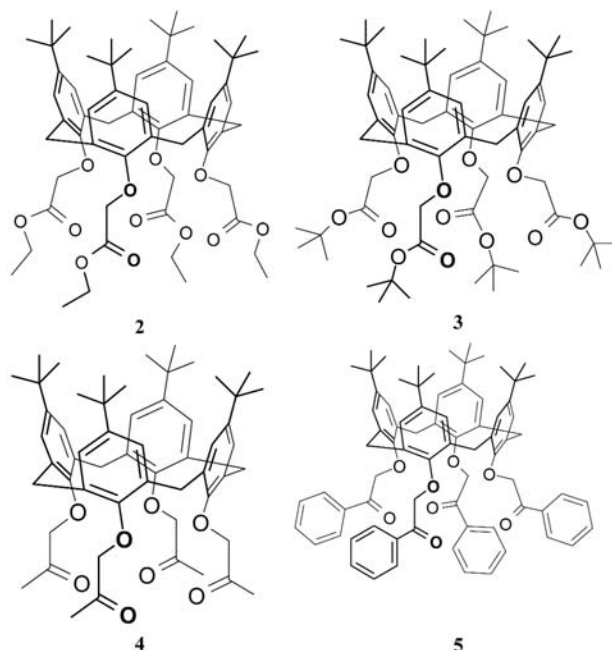
In this study, from the extraction experiments and  $\gamma$ -activity measurements (see Experimental) by means Eq.

(5), the logarithms of the constants  $K_{ex}(M^{2+}, 1\cdot Sr^{2+})$  were determined, as given in Table 1.

Furthermore, with respect to Refs. 35–39, for the extraction constants  $K_{ex}(M^{2+}, Sr^{2+})$  and  $K_{ex}(M^{2+}, 1\cdot Sr^{2+})$  defined above, as well as for the stability constants of the complexes  $1\cdot M^{2+}$  and  $1\cdot Sr^{2+}$  in nitrobenzene saturated with water, denoted by  $\beta_{nb}(1\cdot M^{2+})$  and  $\beta_{nb}(1\cdot Sr^{2+})$ , respectively, one gets

$$\log \beta_{nb}(1\cdot M^{2+}) = \log \beta_{nb}(1\cdot Sr^{2+}) + \log K_{ex}(M^{2+}, 1\cdot Sr^{2+}) - \log K_{ex}(M^{2+}, Sr^{2+}) \quad (6)$$

By using the constants  $\log K_{ex}(M^{2+}, Sr^{2+})$  and  $\log K_{ex}(M^{2+}, 1\cdot Sr^{2+})$  given in Table 1,  $\log \beta_{nb}(1\cdot Sr^{2+}) = 15.2$ ,<sup>40</sup> determined from the distribution of strontium picrate in the water-nitrobenzene system containing the calix[4]arene ligand **1**, and applying Eq. (6), we obtain the stability constants of the complexes  $1\cdot M^{2+}$  ( $M^{2+} = Ca^{2+}, Ba^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, UO_4^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}$ ) in nitrobenzene



**Scheme 2.** Structural formulas of tetraethyl *p*-*tert*-butylcalix[4]arene tetraacetate (abbrev. **2**), tetra-*tert*-butyl *p*-*tert*-butylcalix[4]arene tetraacetate (**3**), tetramethyl *p*-*tert*-butylcalix[4]arene tetraketone (**4**) and tetraphenyl *p*-*tert*-butylcalix[4]arene tetraketone (**5**).

**Table 3.** Stability constants of the  $1 \cdot M^+$  cations ( $M^+ = Li^+, Na^+, K^+, Rb^+, Cs^+, H_3O^+, NH_4^+, Ag^+, Tl^+$ ;  $1 = p$ -tert-butylcalix[4]arene-tetrakis(*N,N*-diethylacetamide)) in nitrobenzene saturated with water at 25 °C.

$M^+$	$Li^+$	$Na^+$	$K^+$	$Rb^+$	$Cs^+$	$H_3O^+$	$NH_4^+$	$Ag^+$	$Tl^+$
$\log \beta_{nb}(1 \cdot M^+)$	10.0 <sup>a</sup>	9.8 <sup>b</sup>	6.1 <sup>c</sup>	7.0 <sup>a</sup>	6.4 <sup>a</sup>	8.1 <sup>d</sup>	6.7 <sup>c</sup>	8.5 <sup>a</sup>	7.1 <sup>a</sup>

<sup>a</sup> Ref. 46; <sup>b</sup> Ref. 47; <sup>c</sup> Ref. 48; <sup>d</sup> Ref. 49; <sup>e</sup> Ref. 50.

saturated with water. These data are also reviewed in Table 1. Thus, the  $\beta_{nb}(1 \cdot M^{2+})$  values from this table indicate that the stability of the complex cation  $1 \cdot M^{2+}$  in water-saturated nitrobenzene increases in the series of  $Sr^{2+} < Cu^{2+} < Ba^{2+} < Zn^{2+} < Ni^{2+} < UO_2^{2+} < Co^{2+} < Mn^{2+} < Cd^{2+} < Ca^{2+} < Pb^{2+}$ .

Finally, stability constants of the complexes  $2 \cdot M^{2+}$ ,  $3 \cdot M^{2+}$ ,  $4 \cdot M^{2+}$  and  $5 \cdot M^{2+}$ , where **2** = tetraethyl *p*-tert-butylcalix[4]arene tetraacetate, **3** = tetra-*tert*-butyl *p*-tert-butylcalix[4]arene tetraacetate, **4** = tetramethyl *p*-tert-butylcalix[4]arene tetraketone, **5** = tetraphenyl *p*-tert-butylcalix[4]arene tetraketone (see Scheme 2) and  $M^{2+} = Ca^{2+}, Sr^{2+}, Ba^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, UO_2^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}$ , in nitrobenzene saturated with water are listed in Table 2. In this context it should be emphasized that the stabilities of the complex cations  $1 \cdot M^{2+}$  determined here in water-saturated nitrobenzene are essentially higher than those of the complexes  $2 \cdot M^{2+}$ ,  $3 \cdot M^{2+}$ ,  $4 \cdot M^{2+}$  and  $5 \cdot M^{2+}$  evaluated previously in this medium,<sup>41–45</sup> as follows from Tables 1 and 2.

In conclusion, Table 3 summarizes stability constants of the complexes  $1 \cdot M^+$ , where  $M^+ = Li^+, Na^+, K^+, Rb^+, Cs^+, H_3O^+, NH_4^+, Ag^+, Tl^+$ , in nitrobenzene saturated with water at 25 °C. From the data given in this table it follows that the stabilities of these univalent complex species  $1 \cdot M^+$  in the considered nitrobenzene medium are substantially lower than those of the divalent metal complexes  $1 \cdot M^{2+}$  studied in the present work (see Table 1). Therefore, from this point of view, the substituted calix[4]arene ligand **1** cannot be considered as a sodium ionophore only,<sup>21</sup> but namely as an ionophore or a strong receptor, respectively, for all the divalent cations summarized in Table 1.

## 4. Acknowledgements

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.

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## Povzetek

S pomočjo ekstrakcijskih eksperimentov in meritev  $\gamma$ -aktivnosti smo v dvofaznem sistemu voda-nitrobenzen določili konstante ekstrakcije za ravnotežje  $M^{2+}(aq) + 1 \cdot Sr^{2+}(nb) \rightleftharpoons 1 \cdot M^{2+}(nb) + Sr^{2+}(aq)$ ; ( $M^{2+} = Ca^{2+}, Ba^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, UO_2^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}$ ;  $1 = p$ -*tert*-butilcalix[4]aren-tetrakis (*N,N*-dietilacetamid); aq = vodna faza, nb = faza nitrobenzena). Določili smo tudi konstante stabilnosti za komplekse  $1 \cdot M^2$  v vodni fazi, nasičeni z nitrobenzenom in ugotovili, da naraščajo v zaporedju  $Cu^{2+} < Ba^{2+} < Zn^{2+} < Ni^{2+} < UO_2^{2+} < Co^{2+} < Mn^{2+} < Cd^{2+} < Ca^{2+} < Pb^{2+}$ .