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ORIGINAL PAPER

Stability constants of some metal cation complexes of tetraphenyl *p-tert*-butylcalix[4]arene tetraketone in nitrobenzene saturated with water

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Abstract From extraction experiments and γ-activity measurements, the exchange extraction constants corresponding to the general equilibrium $M^{2+}(aq) + \mathbf{1} \cdot Sr^{2+}(nb) \rightleftarrows \mathbf{1} \cdot M^{2+}(nb) + Sr^{2+}(aq)$ 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+}; $\mathbf{1}$ = tetraphenyl *p-tert*-butylcalix[4]arene tetraketone; aq = aqueous phase, nb = nitrobenzene phase) were evaluated. Further, the stability constants of the $\mathbf{1} \cdot M^{2+}$ complexes in water-saturated nitrobenzene were calculated; they were found to increase in the cation order Ba^{2+}, $Mn^{2+} < Co^{2+} < Cu^{2+}$, $Ni^{2+} < Zn^{2+}$, Cd^{2+}, $UO_2{}^{2+} < Ca^{2+} < Pb^{2+}$.

Keywords Calixarenes · Macrocycles · Complexation · Metal cations · Stability constants

Introduction

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 properties, calix[*n*]arenes are widely used as the building blocks for the construction of more sophisticated molecular systems. Their unique three-dimensional pre-organization make them very attractive as receptors for complexation of cations, anions, and even neutral molecules. Calix[*n*]arenes find applications as selective binders and carriers, as analytical sensors, as catalysts, and as model structures for biomimetic studies [1, 2].

Recently, the interactions of the H_3O^+ ion with some calix[4]arenes have been investigated [3–7]. On the other hand, in the current work, the solvent extraction of some metal cations into nitrobenzene by use of a synergistic mixture of strontium dicarbollylcobaltate [8] and tetraphenyl *p-tert*-butylcalix[4]arene tetraketone (abbrev. **1**, cf. Scheme 1) has been studied. Moreover, the stability constants of the proved cation complexes $\mathbf{1} \cdot M^{2+}$ ($M^{2+} = Ca^{2+}, Ba^{2+}, Cu^{2+}$, Zn^{2+}, Cd^{2+}, Pb^{2+}, $UO_2{}^{2+}$, Mn^{2+}, Co^{2+}, Ni^{2+}) with the mentioned calix[4]arene ligand **1** in nitrobenzene saturated with water have been determined.

Results and discussion

With regard to the previous results [9–13], the two-phase water–$M(NO_3)_2$ ($M^{2+} = Ca^{2+}$, Ba^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, $UO_2{}^{2+}$, Mn^{2+}, Co^{2+}, Ni^{2+})/nitrobenzene–$Sr(DCC)_2$ extraction system can be described by the following equilibrium (1) with the corresponding exchange extraction constant $K_{ex}(M^{2+}, Sr^{2+})$; aq and nb denote the presence of the species in the aqueous and nitrobenzene phases.

$$M^{2+}(aq) + Sr^{2+}(nb) \rightleftarrows M^{2+}(nb) + Sr^{2+}(aq); \quad K_{ex}(M^{2+}, Sr^{2+}) \qquad (1)$$

For the constant $K_{ex}(M^{2+}, Sr^{2+})$ one can write Eq. (2) where $K^i_{M^{2+}}$ and $K^i_{Sr^{2+}}$ are the individual extraction

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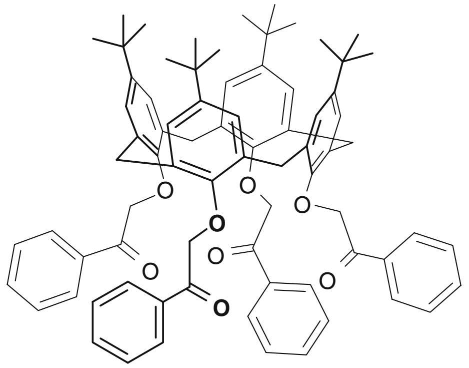

Scheme 1

constants for M^{2+} and Sr^{2+} in the water/nitrobenzene system [9].

$$\log K_{ex}\left(M^{2+}, Sr^{2+}\right) = \log K^{i}_{M^{2+}} - \log K^{i}_{Sr^{2+}} \tag{2}$$

Knowing $\log K^{i}_{Cu^{2+}} = -11.5$, $\log K^{i}_{Zn^{2+}} = -11.6$, $\log K^{i}_{Cd^{2+}} = -11.5$, $\log K^{i}_{Pb^{2+}} = -10.6$, $\log K^{i}_{UO_2^{2+}} = -11.8$, $\log K^{i}_{Mn^{2+}} = -11.1$, $\log K^{i}_{Co^{2+}} = -11.4$, $\log K^{i}_{Ni^{2+}} = -11.6$ [13], $\log K^{i}_{Ba^{2+}} = -10.5$ [12], $\log K^{i}_{Ca^{2+}} = -11.2$, inferred from [9, 10], and $\log K^{i}_{Sr^{2+}} = -10.7$, inferred from [9, 11], the single exchange extraction constants $K_{ex}\left(M^{2+}, Sr^{2+}\right)$ were simply calculated on the basis of Eq. (2). The corresponding data are given in Table 1.

In terms of previous papers [14–17], the two-phase water–$M(NO_3)_2$ ($M^{2+} = Ca^{2+}$, Ba^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, UO_2^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+})/nitrobenzene-**1** (tetraphenyl *p*-*tert*-butylcalix[4]arene tetraketone)-$Sr(DCC)_2$ extraction system (see "Experimental"), chosen for determination of stability of the complex $\mathbf{1} \cdot M^{2+}$ in water-saturated nitrobenzene, can be characterized by the main chemical equilibrium (Eq. 3) to which the equilibrium extraction constant as shown by Eq. (4) corresponds.

$$M^{2+}(aq) + \mathbf{1} \cdot Sr^{2+}(nb) \rightleftarrows \mathbf{1} \cdot M^{2+}(nb) + Sr^{2+}(aq); \quad K_{ex}\left(M^{2+}, \mathbf{1} \cdot Sr^{2+}\right) \tag{3}$$

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

It is necessary to emphasize that **1** is a very hydrophobic ligand, practically present in the nitrobenzene phase only, where this ligand forms the very stable complexes $\mathbf{1} \cdot M^{2+}$ and $\mathbf{1} \cdot Sr^{2+}$ with the mentioned divalent cations. Taking into account the conditions of electroneutrality in the organic and aqueous phases of the system under study, the mass balances of the considered cations at equal volumes of the nitrobenzene and aqueous phases, and the measured equilibrium distribution ratio of strontium, $D_{Sr} = [\mathbf{1} \cdot Sr^{2+}]_{nb}/[Sr^{2+}]_{aq}$, combined with Eq. (4), we obtain the final expression for the exchange extraction constant (Eq. 5); $C^{in,aq}_{M(NO_3)_2}$ is the initial concentration of $M(NO_3)_2$ ($M^{2+} = Ca^{2+}$, Ba^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, UO_2^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}) in the aqueous phase and $C^{in,nb}_{Sr(DCC)_2}$ denotes the initial concentration of $Sr(DCC)_2$ in the organic phase of the system under consideration.

$$K_{ex}\left(M^{2+}, \mathbf{1} \cdot Sr^{2+}\right) = \frac{1}{D_{Sr}} \frac{C^{in,nb}_{Sr(DCC)_2}}{(1 + D_{Sr})C^{in,aq}_{M(NO_3)_2} - C^{in,nb}_{Sr(DCC)_2}} \tag{5}$$

In this study, from the extraction experiments and γ-activity measurements by means of Eq. (5), the logarithms of the constants K_{ex} (M^{2+}, $\mathbf{1} \cdot Sr^{2+}$) were determined, and are given in Table 1.

Table 1 Equilibrium data for the M^{2+} and $\mathbf{1} \cdot M^{2+}$ cations in the two-phase water/nitrobenzene extraction system at 25 °C

Quantity	Ca^{2+}	Sr^{2+}	Ba^{2+}	Cu^{2+}	Zn^{2+}	Cd^{2+}	Pb^{2+}	UO_2^{2+}	Mn^{2+}	Co^{2+}	Ni^{2+}
$\log K^{i}_{M^{2+}}$	−11.2[a]	−10.7[b]	−10.5[c]	−11.5[d]	−11.6[d]	−11.5[d]	−10.6[d]	−11.8[d]	−11.1[d]	−11.4[d]	−11.6[d]
$\log K_{ex}\left(M^{2+}, Sr^{2+}\right)$[e]	−0.5	–	0.2	−0.8	−0.9	−0.8	0.1	−1.1	−0.4	−0.7	−0.9
$\log K_{ex}\left(M^{2+}, 1 \cdot Sr^{2+}\right)$[f]	1.0	–	−0.5	−1.0	−1.0	−0.9	2.7	−1.2	−1.1	−1.2	−1.1
$\log \beta_{nb}\left(1 \cdot M^{2+}\right)$[g]	10.2	8.7[h]	8.0	8.5	8.6	8.6	11.3	8.6	8.0	8.2	8.5

$M^{2+} = Ca^{2+}$, Sr^{2+}, Ba^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, UO_2^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}; **1** = tetraphenyl *p*-*tert*-butylcalix[4]arene tetraketone; for the meaning of the constants see text

[a] Inferred from [9, 10]

[b] Inferred from [9, 11]

[c] Reference [12]

[d] Reference [13, unpublished results]

[e] Calculated from Eq. (2) using data from [9–12] and [13, unpublished results]

[f] Calculated from Eq. (5)

[g] Calculated from Eq. (6) using data from [9–12] and [13, 18, unpublished results]

[h] Reference [18, unpublished results]

Furthermore, with respect to [14–17], for the extraction constants $K_{ex}(\mathrm{M}^{2+}, \mathrm{Sr}^{2+})$ and K_{ex} (M^{2+}, $\mathbf{1} \cdot \mathrm{Sr}^{2+}$) defined above, and for the stability constants of the complexes $\mathbf{1} \cdot \mathrm{M}^{2+}$ and $\mathbf{1} \cdot \mathrm{Sr}^{2+}$ in nitrobenzene saturated with water, denoted by β_{nb} ($\mathbf{1} \cdot \mathrm{M}^{2+}$) and β_{nb} ($\mathbf{1} \cdot \mathrm{Sr}^{2+}$), one obtains Eq. (6).

$$\begin{aligned}\log \beta_{\mathrm{nb}}(\mathbf{1} \cdot \mathrm{M}^{2+}) = {} & \log \beta_{\mathrm{nb}}(\mathbf{1} \cdot \mathrm{Sr}^{2+}) \\ & + \log K_{\mathrm{ex}}(\mathrm{M}^{2+}, \mathbf{1} \cdot \mathrm{Sr}^{2+}) \\ & - \log K_{\mathrm{ex}}(\mathrm{M}^{2+}, \mathrm{Sr}^{2+}) \end{aligned} \qquad (6)$$

By using the constants K_{ex} (M^{2+}, Sr^{2+}) and log K_{ex} (M^{2+}, $\mathbf{1} \cdot \mathrm{Sr}^{2+}$) given in Table 1, log β_{nb} ($\mathbf{1} \cdot \mathrm{Sr}^{2+}$) = 8.7 [18], determined from the distribution of strontium picrate in the water/nitrobenzene extraction system containing the calix[4]arene ligand **1**, and applying Eq. (6), we obtain the stability constants of the complexes $\mathbf{1} \cdot \mathrm{M}^{2+}$ ($\mathrm{M}^{2+} = \mathrm{Ca}^{2+}$, Ba^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, $\mathrm{UO_2}^{2+}$, Mn^{2+}, Co^{2+}, Ni^{2+}) in water-saturated nitrobenzene. These data are summarized in Table 1. Thus, from this table it follows that the stability of the $\mathbf{1} \cdot \mathrm{M}^{2+}$ cationic complex species in the mentioned medium increases in the series Ba^{2+}, $\mathrm{Mn}^{2+} < \mathrm{Co}^{2+} < \mathrm{Cu}^{2+}$, $\mathrm{Ni}^{2+} < \mathrm{Zn}^{2+}$, Cd^{2+}, $\mathrm{UO_2}^{2+} < \mathrm{Sr}^{2+} < \mathrm{Ca}^{2} < \mathrm{Pb}^{2+}$.

Finally, the stability constants of the $\mathbf{2} \cdot \mathrm{M}^{2+}$ cationic complex species, where **2** is tetramethyl *p-tert*-butylcalix[4]arene tetraketone and $\mathrm{M}^{2+} = \mathrm{Sr}^{2+}$, Ba^{2+}, Cd^{2+}, Pb^{2+}, in water-saturated nitrobenzene determined previously [18, 19] are listed in Table 2. From the data presented in Tables 1 and 2 it follows that the stabilities of the $\mathbf{1} \cdot \mathrm{M}^{2+}$ and $\mathbf{2} \cdot \mathrm{M}^{2+}$ complexes ($\mathrm{M}^{2+} = \mathrm{Sr}^{2+}$, Ba^{2+}, Cd^{2+}, Pb^{2+}) for the given M^{2+} cation in the mentioned medium are nearly the same. This means that the $\mathrm{C_6H_5}$ and $\mathrm{CH_3}$ moieties of the respective calix[4]arene ligands **1** and **2** obviously have only very little influence upon the stability of the $\mathbf{1} \cdot \mathrm{M}^{2+}$ and $\mathbf{2} \cdot \mathrm{M}^{2+}$ species ($\mathrm{M}^{2+} = \mathrm{Sr}^{2+}$, Ba^{2+}, Cd^{2+}, Pb^{2+}), in which the cation M^{2+} is placed in the coordination cavity formed by four lower-rim groups –O–CH$_2$–CO– of the corresponding calix[4]arene ligand.

Experimental

Compound **1** was synthesized by the procedure published elsewhere [20]. Cs dicarbollylcobaltate, CsDCC, was supplied by Katchem, Řež, Czech Republic. A nitrobenzene solution of hydrogen dicarbollylcobaltate (HDCC) [8] was prepared from CsDCC by the method described elsewhere [21]. The other chemicals used (Lachema, Brno, Czech Republic) were of reagent-grade purity. The equilibration of the nitrobenzene solution of HDCC with stoichiometric $\mathrm{Sr(OH)_2}$, which was dissolved in an aqueous solution of $\mathrm{Sr(NO_3)_2}$ (0.2 M), yielded the corresponding $\mathrm{Sr(DCC)_2}$ solution in nitrobenzene. The radionuclide $^{85}\mathrm{Sr}^{2+}$ (DuPont, Belgium) was of standard radiochemical purity.

The extraction experiments were carried out in 10 cm^3 glass test-tubes with polyethylene stoppers: 2 cm^3 of an aqueous solution of $\mathrm{M(NO_3)_2}$ ($\mathrm{M}^{2+} = \mathrm{Ca}^{2+}$, Ba^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, $\mathrm{UO_2}^{2+}$, Mn^{2+}, Co^{2+}, Ni^{2+}) of concentration in the range 1×10^{-3} to 1×10^{-2} M and micro amounts of $^{85}\mathrm{Sr}^{2+}$ were added to 2 cm^3 of a nitrobenzene solution of **1** and $\mathrm{Sr(DCC)_2}$, whose initial concentrations also varied from 1×10^{-3} to 1×10^{-2} M (in all experiments, the initial concentration of **1** in nitrobenzene, $C_1^{\mathrm{in,nb}}$, was always equal to the initial concentration of $\mathrm{Sr(DCC)_2}$ in this medium, $C_{\mathrm{Sr(DCC)_2}}^{\mathrm{in,nb}}$). The test-tubes filled with the solutions were shaken for 24 h at 25 ± 1 °C, using a laboratory shaker. The phases were then separated by centrifugation. Afterwards, 1 cm^3 samples were taken from each phase and their γ-activities were measured using a well-type NaI(Tl) scintillation detector connected to a γ-analyser NK/350 (Gamma, Budapest, Hungary).

The equilibrium distribution ratio of strontium, D_{Sr}, was determined as the ratio of the measured radioactivities of $^{85}\mathrm{Sr}^{2+}$ in the nitrobenzene and aqueous samples.

Table 2 Stability constants of the $\mathbf{2} \cdot \mathrm{M}^{2+}$ cations ($\mathrm{M}^{2+} = \mathrm{Sr}^{2+}$, Ba^{2+}, Cd^{2+}, Pb^{2+},where **2** = tetramethyl *p-tert*-butylcalix[4]arene tetraketone) in nitrobenzene saturated with water at 25 °C

M^{2+}	Sr^{2+}	Ba^{2+}	Cd^{2+}	Pb^{2+}
log β_{nb} ($\mathbf{2} \cdot \mathrm{M}^{2+}$)	8.8[a]	8.3[b]	8.5[b]	11.2[b]

[a] Reference [18, unpublished results]

[b] Reference [19]

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