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Journal of the Serbian Chemical Society

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J. Serb. Chem. Soc. *73* (12) 1181–1186 (2008) UDC 544.354–128.4+547.545/.548:66.061:532.74
JSCS–3797 *Short communication*

SHORT COMMUNICATION

Solvent 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 using strontium dicarbollylcobaltate and tetra-*tert*-butyl *p*-*tert*-butylcalix[4]arene tetraacetate

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(Received 4 February, revised 26 May 2008)

Abstract: The exchange extraction constants corresponding to the general equilibrium $M^{2+}(aq) + SrL^{2+}(nb) \rightleftarrows ML^{2+}(nb) + Sr^{2+}(aq)$ occurring 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+} or Ni^{2+}; L = tetra-*tert*-butyl *p*-*tert*-butylcalix[4]arene tetraacetate; aq = aqueous phase; nb = nitrobenzene phase) were evaluated from extraction experiments and γ-activity measurements. Furthermore, the stability constants of the ML^{2+} complexes in water saturated nitrobenzene were calculated; they were found to increase in the cation order $Ba^{2+} < Mn^{2+} < Pb^{2+}$, $Co^{2+} < Cu^{2+}$, $Zn^{2+} < Cd^{2+}$, $Ni^{2+} < UO_2^{2+} < Ca^{2+}$.

Keywords: divalent cations; calix[4]arene compound; extraction and stability constants; water–nitrobenzene system.

INTRODUCTION

The dicarbollylcobaltate anion and some of its halogen derivatives are very useful reagents for the extraction of alkali metal cations (especially Cs^+), and also, in the presence of polyoxyethylene compounds, for the extraction of Sr^{2+} and Ba^{2+} from an aqueous solution into a polar organic phase, both under laboratory conditions for purely theoretical or analytical purposes,[1] and on the technological scale for the separation of some high-activity isotopes in the reprocessing of spent nuclear fuel and acidic radioactive waste.[2–4]

Calix[*n*]arenes are a well-known family of macrocyclic molecules with many potential applications in various branches of chemistry. Due to their simple one-pot preparation, easy derivatization and unique complexation abilities, calix[*n*]arenes

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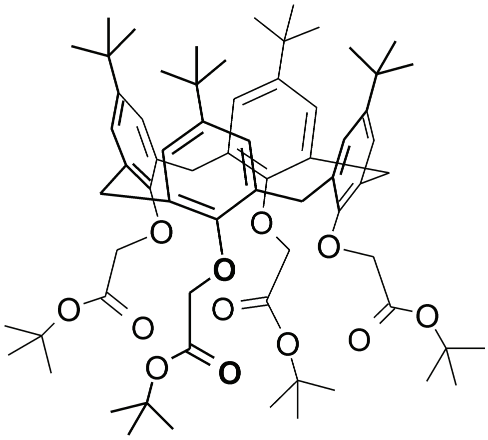
doi: 10.2298/JSC0812181M

are widely used as 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.[5,6] 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.[7–15]

In the present communication, the solvent 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 using a synergistic mixture of strontium dicarbollylcobaltate and tetra-*tert*-butyl *p*-*tert*-butylcalix[4]arene tetraacetate (see Scheme 1), similar to a previous study[16], was investigated. Furthermore, the stability constants of the proved divalent cation complexes with the mentioned calix[4]arene ligand in the organic phase of the water–nitrobenzene extraction system were determined.



Scheme 1. Structural formula of tetra-*tert*-butyl *p*-*tert*-butylcalix[4]arene tetraacetate (abbrev. L).

EXPERIMENTAL

Tetra-*tert*-butyl *p*-*tert*-butylcalix[4]arene tetraacetate was synthesized using the procedure published by Arnaud-Neu *et al.*[9] Cesium 3,3'-*commo*-bis (undecahydro-1,2-dicarba-3-cobalta-*closo*-dodecabor)ate, $Cs^+\{[\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}]Co(III)\}^-$ (also called cesium dicarbollylcobaltate, Cs(DCC), was supplied by Katchem, Řež, Czech Republic. A nitrobenzene solution of hydrogen dicarbollylcobaltate (HDCC)[1] was prepared from CsDCC by the method described elsewhere.[17] The other employed chemicals were of reagent grade purity (Lachema, Brno, Czech Republic). The equilibration of the nitrobenzene solution of HDCC with stoichiometric $Sr(OH)_2$ yielded the corresponding $Sr(DCC)_2$ solution in nitrobenzene. The radionuclide $^{85}Sr^{2+}$ (DuPont, Belgium) was of standard radiochemical purity.

The extraction experiments were performed in 10 ml glass test-tubes covered with polyethylene stoppers: 2.0 ml of an aqueous solution 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+} or Ni^{2+}) of concentration in the range from 1.0×10^{-3} to 1.0×10^{-2}

mol/l and micro amounts of $^{85}Sr^{2+}$ were added to 2.0 ml of a nitrobenzene solution of tetra-*tert*-butyl *p-tert*-butylcalix[4]arene tetraacetate and $Sr(DCC)_2$, the initial concentrations of which also varied from 1.0×10^{-3} to 1.0×10^{-2} mol/l (in all experiments, the initial concentration of tetra-*tert*-butyl *p-tert*-butylcalix[4]arene tetraacetate in nitrobenzene, $c_{L}^{in,nb}$, was always equal to the initial concentration of $Sr(DCC)_2$ in this medium, $c_{Sr(DCC)_2}^{in,nb}$). 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, 1.0 ml samples were taken from each phase and their γ-activities were measured using a well-type NaI(T1) scintillation detector connected to a γ-analyzer NK/350 (Gamma, Budapest, Hungary).

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

RESULTS AND DISCUSSION

According to the results of previous papers,[1,18–21] 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 general equilibrium:

$$M^{2+}(aq) + Sr^{2+}(nb) \rightleftarrows M^{2+}(nb) + Sr^{2+}(aq) \qquad (1)$$

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, respectively. For the constant $K_{ex}(M^{2+},Sr^{2+})$, one can write:

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

where $K_{M^{2+}}^{i}$ and $K_{Sr^{2+}}^{i}$ are the individual extraction constants for M^{2+} and Sr^{2+}, respectively, in the water–nitrobenzene system.[18] Knowing $\log K_{Ca^{2+}}^{i} = -11.2$,[18,19] $\log K_{Ba^{2+}}^{i} = -10.5$,[21] $\log K_{Cu^{2+}}^{i} = \log K_{Cd^{2+}}^{i} = -11.5$,[22] $\log K_{Zn^{2+}}^{i} = \log K_{Ni^{2+}}^{i} = -11.6$,[22] $\log K_{Pb^{2+}}^{i} = -10.6$,[22] $\log K_{UO_2^{2+}}^{i} = -11.8$,[22] $\log K_{Mn^{2+}}^{i} = -11.1$,[22] $\log K_{Co^{2+}}^{i} = -11.4$[22] and $\log K_{Sr^{2+}}^{i} = -10.7$,[18,20] the single exchange extraction constants $K_{ex}(M^{2+}, Sr^{2+})$ were simply calculated from Eq. (2). The corresponding data are given in Table I.

TABLE I. Equilibrium data for the M^{2+} and ML^{2+} cations in the two-phase water–nitrobenzene extraction system at 25 °C ($M^{2+} = Ca^{2+}$, Sr^{2+}, Ba^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, UO_2^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}; L = tetra-*tert*-butyl *p-tert*-butylcalix[4]arene tetraacetate; for the meaning of the constants, see text)

Quantity	Ca^{2+}	Sr^{2+}	Ba^{2+}	Cu^{2+}	Zn^{2+}	Cd^{2+}	Pb^{2+}	UO_2^{2+}	Mn^{2+}	Co^{2+}	Ni^{2+}
$\log K_{M^{2+}}^{i}$	–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]
$\log K_{ex}(M^{2+},Sr^{2+})$[e]	–0.50	–	0.20	–0.80	–0.90	–0.80	0.10	–1.1	–0.40	–0.70	–0.90
$\log K_{ex}(M^{2+},SrL^{2+})$[f]	1.0	–	–0.70	–1.1	–1.2	–1.0	–0.30	–1.0	–1.0	–1.1	–1.1
$\log \beta_{nb}(ML^{2+})$[g]	8.6	7.1[h]	6.2	6.8	6.8	6.9	6.7	7.2	6.5	6.7	6.9

[a] Inferred from Refs. 18 and 19; [b] inferred from Refs. 18 and 20; [c] Ref. 21; [d] Ref. 22; [e] calculated from Eq. (2) using data from Refs. 18–22; [f] calculated from Eq. (5); [g] calculated from Eq. (6) using data from Refs. 18–22; [h] determined by the method described in detail in Ref. 23

Previous results[24–26] showed that 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+} or Ni^{2+})–nitrobenzene–L (L = = tetra-*tert*-butyl *p*-*tert*-butylcalix[4]arene tetraacetate)–$Sr(DCC)_2$ extraction system (see Experimental), chosen for the determination of stability of the ML^{2+} complexes in nitrobenzene saturated with water, can be characterized by the main chemical equilibrium (3):

$$M^{2+}(aq) + SrL^{2+}(nb) \rightleftarrows ML^{2+}(nb) + Sr^{2+}(aq) \tag{3}$$

with the general equilibrium extraction constant $K_{ex}(M^{2+}, SrL^{2+})$ given by:

$$K_{ex}(M^{2+},SrL^{2+}) = \frac{[ML^{2+}]_{nb}[Sr^{2+}]_{aq}}{[M^{2+}]_{aq}[SrL^{2+}]_{nb}} \tag{4}$$

It is necessary to emphasize that tetra-*tert*-butyl *p*-*tert*-butylcalix[4]arene tetraacetate is a very hydrophobic ligand, practically present in the nitrobenzene phase only, where it forms very stable complexes ML^{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 divalent cations studied at equal volumes of the nitrobenzene and aqueous phases, as well as the measured equilibrium distribution ratio of strontium, D_{Sr} = = $[SrL^{2+}]_{nb}/[Sr^{2+}]_{aq}$, combined with Eq. (4), the final expression for $K_{ex}(M^{2+}, SrL^{2+})$ is obtained in the form:

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

where $c^{in,aq}_{M(NO_3)_2}$ 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+} or Ni^{2+}) in the aqueous phase of the system under consideration.

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

Moreover, according to previous studies,[24–26] for the extraction constants $K_{ex}(M^{2+}, Sr^{2+})$ and $K_{ex}(M^{2+}, SrL^{2+})$ defined above, as well as for the stability constants of the complexes ML^{2+} and SrL^{2+} in nitrobenzene saturated with water, denoted by $\beta_{nb}(ML^{2+})$ and $\beta_{nb}(SrL^{2+})$, respectively, one obtains:

$$\begin{aligned} \log\beta_{nb}(ML^{2+}) = \log\beta_{nb}(SrL^{2+}) + \log K_{ex}(M^{2+},SrL^{2+}) - \\ - \log K_{ex}(M^{2+},Sr^{2+}) \end{aligned} \tag{6}$$

Finally, using the values of log $K_{ex}(M^{2+},Sr^{2+})$ and log $K_{ex}(M^{2+},SrL^{2+})$ given in Table I, log β_{nb} (SrL^{2+}) = 7.1, determined from the distribution of strontium picrate in the water–nitrobenzene system containing the considered calix[4]arene ligand by the method described in detail previously,[23] and applying Eq. (6), the stability constants of the ML^{2+} complexes in water-saturated nitrobenzene are obtained. These data are also summarized in Table I. Thus, the β_{nb} (ML^{2+}) values from this table indicate that the stability of the ML^{2+} cationic complex species in the mentioned medium increases in the series $Ba^{2+} < Mn^{2+} < Pb^{2+}$, $Co^{2+} < < Cu^{2+}$, $Zn^{2+} < Cd^{2+}$, $Ni^{2+} < Sr^{2+} < UO_2^{2+} < Ca^{2+}$.

Acknowledgements. The presented work was supported by the Czech Ministry of Education, Youth and Sports, Projects MSM 4977751303 and MSM 6076137307.

ИЗВОД

ЕКСТРАКЦИЈА Ca^{2+}, Ba^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, UO_2^{2+}, Mn^{2+}, Co^{2+} И Ni^{2+} СТРОНЦИЈУМ ДИКАРБОНИЛ КОБАЛТАТА И ТЕТРА-*tert*-БУТИЛ-*p*-*tert*-БУТИЛКАЛИКС[4]АРЕН ТЕТРААЦЕТАТА У РАСТВОР НИТРОБЕНЗЕНА

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На основу измерених коефицијената активности γ, добијених из екстракционих мерења, одређена је константа екстракционе равнотеже на основу опште једначине $M^{2+}(aq) + SrL^{2+}(nb) \rightleftarrows ML^{2+}(nb) + Sr^{2+}(aq)$, где су: $M^{2+} = Ca^{2+}$, Ba^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, UO_2^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}; L = тетра-*tert*-бутил-*p*-*tert*-бутилкаликс[4]арен тетраацетат; aq = водена фаза, nb = фаза нитробензена. Одредјене константе стабилности комплекса ML^{2+} у раствору нитробензена засићеног водом расту према катјону у комплексу по следећем редоследу: $Ba^{2+} < < Mn^{2+} < Pb^{2+}$, $Co^{2+} < Cu^{2+}$, $Zn^{2+} < Cd^{2+}$, $Ni^{2+} < UO_2^{2+} < Ca^{2+}$.

(Примљено 4. фебруара, ревидирано 26. маја 2008)

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