Interaction of the thallium cation with 1,3-*alternate*-25,27-bis(1-octyloxy)calix[4]arene-crown-6: Experimental and theoretical study

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HIGHLIGHTS

- Stability of the $Tl^+ \cdot 1$,3-*alternate*-25,27-bis(1-octyloxy)calix[4]arene-crown-6 complex was determined.
- The quantum mechanical DFT calculations were carried out.
- Structures A and B of the resulting cationic complex species were predicted.

GRAPHICAL ABSTRACT
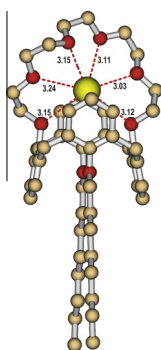
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ABSTRACT

From extraction experiments and γ-activity measurements, the extraction constant corresponding to the equilibrium Tl^+ (aq) + $\mathbf{1} \cdot Cs^+$ (nb) $\Leftrightarrow$ $\mathbf{1} \cdot Tl^+$ (nb) + Cs^+ (aq) taking place in the two–phase water–nitrobenzene system ($\mathbf{1}$ = 1,3-*alternate*-25,27-bis(1-octyloxy)calix[4]arene-crown-6; aq = aqueous phase, nb = nitrobenzene phase) was evaluated as $\log K_{ex}$ (Tl^+, $\mathbf{1} \cdot Cs^+$) = -2.1 ± 0.1. Further, the stability constant of the $\mathbf{1} \cdot Tl^+$ complex in nitrobenzene saturated with water was calculated for a temperature of 25 °C: $\log \beta_{nb}(\mathbf{1} \cdot Tl^+)$ = 11.6 ± 0.2. Finally, by using quantum mechanical DFT calculations, the most probable structures A and B of the cationic complex species $\mathbf{1} \cdot Tl^+$, which are obviously in a dynamic equilibrium, were indicated. In both of these structures of the resulting $\mathbf{1} \cdot Tl^+$ complex, the "central" cation Tl^+ is bound by eight strong bond interactions to six oxygen atoms from the 18-crown-6 moiety and to two carbons of the respective two benzene rings of the parent ligand $\mathbf{1}$ via cation-π interaction.

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1. 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 [2–9], and on the technological scale for the separation of some high-activity isotopes in the reprocessing of spent nuclear fuel and acidic radioactive waste [10–12].

Calixarenes are macrocyclic compounds which are not only easily available on a large scale, but also offer nearly boundless possibilities for chemical modification [13]. This makes them highly attractive as the building blocks for more sophisticated and

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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 [14], but also elegantly demonstrate the potential of these compounds [15]. Calixarenes find applications as selective binders and carriers, as analytical sensors, as catalysts and model structures for biomimetic studies [16].

New cesium selective extractants especially from the calix[4]arene-crown-6 and calix[4]arene-bis(crown-6) families have been introduced [17–23]. The corresponding crystal structures of model complexes with cesium salts have demonstrated a significant π-interaction between the facing aromatic rings and the Cs^+ guest cation [17–19]. Besides, the calix[4]arene-crown-6 family of the mentioned compounds gives Cs^+/Na^+ separation factors exceeding 10^4 [18].

In the current work, the solvent extraction of the Tl^+ cation into nitrobenzene by using a synergistic mixture of cesium dicarbollylcobaltate (CsDCC) and 1,3-alternate-25,27-bis(1-octyloxy)calix[4]arene-crown-6 (abbrev. **1**; see Scheme 1) was studied. Moreover, the stability constant of the cationic complex species **1**·Tl^+ in the organic phase of the water–nitrobenzene extraction system was determined. Finally, applying quantum mechanical DFT calculations, the most probable structures of the considered **1**·Tl^+ complex were predicted on the basis of the thorough conformational analysis (i. e., different initial mutual positions of the ligand **1** and the Tl^+ cation were considered during the geometry optimization) and the respective vibrational frequency calculations. It is apparent that these structures may be an important contribution to the theoretical study of calixarenes.

2. 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. [24]. The other chemicals used (Lachema, Brno, Czech Republic) were of reagent grade

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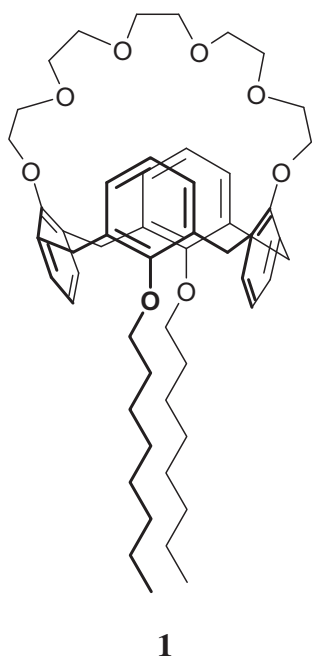
Scheme 1. Structural formula of 1,3-alternate-25,27-bis(1-octyloxy)calix[4]arene-crown-6 (abbrev. **1**).

purity. The radionuclide $^{137}Cs^+$ was purchased from Techsnaveksport, Russia; its radionuclidic purity was 99.9%.

The extraction experiments were carried out in 10 mL glass test-tubes with polyethylene stoppers: 2 mL of an aqueous solution of $TlNO_3$ of the concentration in the range from 1×10^{-3} to 5×10^{-3} M and 10 kBq of $^{137}Cs^+$ were added to 2 mL of a nitrobenzene solution of **1** and CsDCC, whose initial concentrations varied also from 1×10^{-3} to 5×10^{-3} M (in all experiments, the initial concentration of **1** in nitrobenzene, $C_1^{in,nb}$, was equal to the initial concentration of CsDCC in this medium, $C_{CsDCC}^{in,nb}$). The test-tubes filled with the solutions were shaken for 5 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 cesium, D_{Cs}, were determined as the ratios of the corresponding measured radioactivities of $^{137}Cs^+$ in the nitrobenzene and aqueous samples.

3. Results and discussion

3.1. Extraction experiments

Regarding the results of previous papers [1,25,26], the two-phase water–$TlNO_3$–nitrobenzene–cesium dicarbollylcobaltate (CsDCC) extraction system can be described by the following equilibrium

$$Tl^+(aq) + Cs^+(nb) \Longleftrightarrow Tl^+(nb) + Cs^+(aq); \quad K_{ex}(Tl^+, Cs^+) \qquad (1)$$
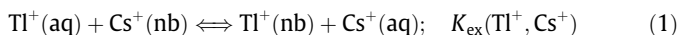
with the corresponding exchange extraction constant K_{ex} (Tl^+, Cs^+); aq and nb denote the presence of the species in the aqueous and nitrobenzene phases, respectively. For the constant K_{ex} (Tl^+, Cs^+) one can write [1,25,26]

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

where $K_{Tl^+}^i$ and $K_{Cs^+}^i$ are the individual extraction constants for Tl^+ and Cs^+, respectively, in the water–nitrobenzene system [25,26]. Knowing the values of $\log K_{Tl^+}^i = -3.4$ [26] and $\log K_{Cs^+}^i = -2.7$ [25], the exchange extraction constant K_{ex} (Tl^+, Cs^+) was simply calculated from Eq. (2) as $\log K_{ex}$ (Tl^+, Cs^+) = −0.7.

Previous results [27–31] indicated that the two-phase water–$TlNO_3$–nitrobenzene–**1** (1,3-alternate-25,27-bis(1-octyloxy)calix[4]arene-crown-6)–CsDCC extraction system (see Section 2), chosen for determination of the stability constant of the **1**·Tl^+ complex in nitrobenzene saturated with water, can be characterized by the main chemical equilibrium

$$Tl^+(aq) + \mathbf{1} \cdot Cs^+(nb) \Longleftrightarrow \mathbf{1} \cdot Tl^+(nb) + Cs^+(aq); \quad K_{ex}(Tl^+, \mathbf{1} \cdot Cs^+) \qquad (3)$$
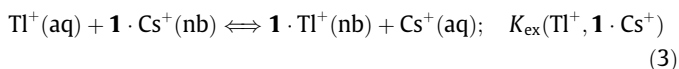
with the respective equilibrium extraction constant K_{ex} (Tl^+, **1**·Cs^+):

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

It is necessary to emphasize that **1** is a considerably hydrophobic ligand, practically present in the nitrobenzene phase only, where this ligand forms – with Tl^+ and Cs^+ – the very stable complexes **1**·Tl^+ and **1**·Cs^+, as given below.

Taking into account the conditions of electroneutrality in the organic and aqueous phases of the system under study, the mass balances of the Tl^+ and Cs^+ cations studied at equal volumes of the nitrobenzene and aqueous phases, as well as the measured equilibrium distribution ratio of cesium, $D_{Cs} = [\mathbf{1} \cdot Cs^+]_{nb}/[Cs^+]_{aq}$,